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# Principles of Chemistry



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# PRINCIPLES *of Chemistry*

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BY

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## *Preface to Fourth Edition*

The fourth revision of this book has been made in order to include improvements in methods of presentation discovered by myself and my colleagues during the interval since the last edition and also to bring certain portions up to date in view of recent progress in physics and chemistry. Examples of the former will, I trust, be noticed here and there throughout the text by teachers familiar with the previous edition. An innovation which I hope will be much appreciated is the printing in smaller type of material which is intended primarily to satisfy the eager curiosity displayed by many bright students, even in an elementary course, while at the same time smoothing the path for the more plodding student who has all he can do to digest the fundamentals.

Scientific progress has made necessary an extensive revision of the chapter on the constitution of the atom, as well as Chapter V, "The Relation of Chemical and Physical Behavior to Atomic Structure." I am greatly indebted to my colleague, Dr. W. F. Libby, for the revision of the former chapter, for which he is eminently fitted by reason both of his clear powers of exposition and his active research in nuclear chemistry.

My own research in the field of solubility and the importance of the subject in nearly all branches of natural science have suggested the addition of a new chapter containing an elementary exposition of a few of the basic ideas connected with this field. It is a chapter which is designed, like the sections in fine print, for voluntary reading rather than compulsory assignment.

Other changes include the addition of sections on other systems of acids and bases, the rôle of activation in deter-

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mining reaction velocities, the use of the terms "oxidation number" and "coördination number" in place of the term "valence," which has been used so extensively in both senses as to be often more or less ambiguous.

The earlier editions of this book were written with the intent to provide discussions of important topics boiled down to their bare essentials, leaving to teachers and to collateral reading the trimmings and flavorings necessary to make the course attractive as a whole. In the present revision I have departed to some extent from this plan and without, I hope, introducing mere padding, have inserted passages here and there designed to assist the student in better methods of study or to give a fuller idea of the scientific method, with hints regarding its application to the complex problems encountered outside the immediate realm of physical science.

J. H. H.

BERKELEY CALIFORNIA  
December, 1939



## *Preface to Third Edition*

In the six years that have elapsed since preparing the second edition of this book, experience in its use has brought to light places where the presentation of certain topics could be markedly improved; the development of our knowledge concerning atomic structure and its connection with chemical behavior has suggested a much fuller correlation thereof with the fundamental questions of chemical behavior such as stability, acid and basic character of hydroxides and solubility; finally, the appearance of the *Reference Book of Inorganic Chemistry*, by Latimer and Hildebrand and the revision of the laboratory manual entitled *A Course in General Chemistry*, by Bray and Latimer, indicated the desirability of bringing up to date all three of these books, which are intended for simultaneous use. It was not expected, when our plan of instruction was first made available for general use, that it would attain immediate popularity. We were confident, however, that it was laying a foundation which would prove sound as students went on into further scientific work. The continual increase of its use in other institutions over a period of years has been very encouraging. The author hopes that the improvements made in this new edition will further enhance this usefulness.

The author has frequently heard the criticism that our plan of instruction is too difficult for students in the average class. It may be of interest to some readers to have a word of explanation regarding our own procedure. We deliberately "expose" the students to far more material than most of them can assimilate. This proves to be a great stimulus to the brilliant students, whose capacity for assimilation seems almost unlimited. It is very gratifying to find how many in our recitation sections eagerly ask ques-

tions that would do credit to graduate students. Of course, we segregate the best students so that they are free to do this. In order, however, not to set an impossible task before the mediocre student, who should not be made to fail if he acquires the main fundamentals of the course, we give questions involving a wide range of difficulty, assigning the major credit to the easier questions. A sample of our weekly quiz follows:

1. Write the equation for the main reaction, if any occurs, in each of the following experiments:

- (1) 0.1M solutions of  $\text{CaCl}_2$  and  $\text{NaOH}$  are mixed;
- (2) " " "  $\text{CaCl}_2$  and  $\text{NH}_4\text{OH}$  are mixed;
- (3) 1 gram-atom of  $\text{Ca}$  is placed in 500 cc. of water;
- (4) 0.1M- $\text{NaHCO}_3$  is mixed with 0.1M- $\text{NaOH}$ ;
- (5) an excess of  $\text{CO}_2$  is passed into 0.1M- $\text{Na}_2\text{CO}_3$ .

Credit 50

2. Give an important use for each of the following: (1)  $\text{Na}_2\text{B}_4\text{O}_7$  (2)  $\text{Mg}$  (3)  $\text{NaHCO}_3$  (4)  $\text{Al}_2(\text{SO}_4)_3$  (5)–(8)  $\text{Al}$  (4 uses) (9)  $\text{Ca}(\text{OH})_2$  (10) an alloy of copper and tin. State so far as you can the property upon which each use principally depends.

Credit 30

3. If it requires 100 cc. of an unknown acid solution to dissolve 0.8 g. of  $\text{Mg}$ , what is the concentration of the acid? ( $\text{Mg} = 24.0$ ). Decide what unit of concentration should be used.

Credit 10

4.  $\text{HAc}$  is a stronger acid than  $\text{H}_2\text{CO}_3$  yet 1M- $\text{NaAc}$  shows more color with phenolphthalein than 1M- $\text{NaHCO}_3$ . Explain.

Credit 10

(Time, 40 Minutes)

It will be seen that a student who is not hopelessly dull or lazy can readily learn enough to answer the first question or two, which will enable him to pass. Indeed, he is warned not to hurry through these questions for the sake of attempting the last question, which is probably quite beyond his ability. The able student, however, finds in the latter part of the quiz questions that try his mettle and require him to extend himself in order to get the high grade of which he is capable. This scheme is cordially recommended to instructors who wish to develop students of exceptional

ability without giving a disproportionate number of very low grades.

I am indebted to Professor W. S. Morley for three of the metallographic photographs.

J. H. H.

BERKELEY, CALIFORNIA  
March, 1932





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# Principles of Chemistry





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# Chapter I

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## *Kinds of Matter*

1. **What Is Chemistry?** Anyone setting out on a journey under the guidance of another naturally likes to know where he is going. The answer to this curiosity, in the case of an excursion into a science, usually takes the form of a definition. The result of this, however, is often to lead the beginner to feel satisfied with merely committing to memory a few inadequate words about a field of study entirely too large and complicated to be so compressed. Measurable quantities such as length, velocity, density, can, it is true, be simply defined, but any attempt to give in a single sentence an adequate idea of chemistry may fall as far short as would an attempt to describe in a few words the "infinite variety" of a certain example of feminine charm. Moreover, it might be dangerous in either case for one to underestimate his ignorance. It is important to know but it is equally important to recognize when one does not know. It might be profitable to predict the course of the stock market but since this is impossible it is very desirable to recognize the fact.

2. In reply to the question, what is chemistry, we shall attempt to give at this stage only a very incomplete idea of its scope, but one which should continually expand as the course progresses. This distrust for definitions may seem to the reader inconsistent with calls for definitions that will be found among the exercises following the chapters of this book. The intention in such cases is that you should con-

struct a definition by relying upon your ability to express in clear, concise English, whatever degree of comprehension of the topic you may have attained. If you seek to ransack your memory you have quite missed the point.

3. Various aspects of the material things we see about us may attract our attention, such as the uses to which they may be put, the beauty of form or color they may possess, or the materials of which they are made. The last only is the immediate concern of chemistry. Two vases may have nothing in common from an artistic standpoint, and a vase and a plate may serve entirely different purposes, and yet, from a chemical point of view, all of them may be essentially identical by reason of the material, porcelain, of which they are made. Chemistry does not concern itself with articles or objects, as typified by such words as chair, pen, bottle, nail, wire, but rather with the **substances** or materials out of which these and other objects may be made, as typified by such words as wood, glass, iron, copper, clay, sugar. One task of the chemist is to ascertain all of the qualities or **properties** of every kind of matter, so that the vast number of different kinds may be recognized and distinguished from each other.

Another task of the chemist is to determine how these substances may be obtained, or, when obtained, how they may be preserved. They do not usually occur in a free state in Nature. Iron, for example, is found but rarely in the free state, and must be obtained from iron ores, by heating them with coke or charcoal in a blast furnace. It is, of course, important to know how much coke to use with a given amount of ore, and how much iron should be obtained from the ore, because the cost of iron is partly determined by these factors. The chemist, therefore, must be concerned not only with iron, its nature and properties, but also with the conditions necessary for getting it from its ores, the quantities of the materials involved in the process, and how to prevent loss by corrosion.

The housewife, in making biscuits with the aid of baking soda and sour milk, finds that if too little soda is used the biscuits will not be "light," whereas if too much soda is used they will be yellow, and the taste will be impaired. She should therefore know not only that when soda and sour milk are mixed they give a gas that will make the dough porous, but also how to adjust the relative amounts necessary for the best results.

4. In the processes just referred to, it is obvious that new kinds of matter have been produced. The iron ore and the coke are quite evidently different stuff from iron. The sour milk loses its sour taste when mixed with sufficient soda, and a gas is evolved quite different from either of the previous materials. Any such change, in which the kind of matter is altered, is called a chemical change, or a **chemical reaction**. When iron is drawn into wire, or made into nails, it is still iron and no chemical change has taken place, but when it rusts it is no longer iron but a brown powder very different from iron. When marble is cut into various shapes it is still marble, whether in the form of a statue, a table top or a building block, possessing all of the characteristics by which we recognize it as marble. If, however, it is heated to a high temperature, it changes in appearance and loses weight, becoming a new substance, quicklime. This again is a chemical reaction. A further chemical reaction takes place if water comes in contact with the quicklime. The color changes from light gray to white, heat is evolved, the mass swells and falls apart to a powder, or, if water is in excess, forms a paste. The resulting material is called slaked lime, a substance whose properties are different from those of marble or quicklime.

5. Often we direct our attention, in dealing with chemical reactions, not so much to the nature of the substances involved, or to their relative amounts, as to the energy used up or liberated by the process. When oil burns it unites with something from the air, as we must infer from the

necessity of an air supply, and forms gaseous products, which ordinarily do not attract our attention except for the necessity of providing for their escape. The most important aspect of such a reaction is the energy made available for light, heat or power. In a dry cell zinc is used up and electrical energy is obtained. The question as to what becomes of the zinc is overshadowed by the question as to how much electrical energy is obtainable from a definite amount of zinc.

6. We see, then, that **chemistry is concerned with substances and their properties; with the changes or reactions whereby other substances are formed; with the conditions necessary for bringing about or preventing these reactions; and with the relative amounts of matter and energy involved.**

7. Various motives may lead one to study chemistry. More or less knowledge of the subject is essential for agriculture, engineering in all its branches, medicine, the biological sciences and most manufacturing industries. Again, all persons whose minds are active feel lively curiosity concerning their environment. This environment is physical and chemical as well as social and economic. Again, chemistry if studied properly as a science gives unsurpassed training in the **scientific method**, one of the major intellectual achievements of mankind. Chemistry, first of all, has progressed much farther than certain other sciences beyond the era of mere description and classification; second, it shares with physics and astronomy a good deal of mathematical rigor, while presenting at the same time phenomena too complicated, as yet, for mathematical treatment and which must be dealt with by more qualitative methods such as are largely characteristic of biology. The scientific method, like chemistry itself, is not subject to brief, precise definition but it includes the planning and performing of experiments carefully designed to reveal facts



and relationships; the use of the imagination to form hypotheses, along with scrupulous care and honesty in subjecting them to the tests both of facts and logic. Such training has both moral and intellectual value and although it is difficult for man to transfer the lessons he learns from one realm to another, nevertheless the problems presented in other fields, particularly the social, political and economic, are so pressing and complicated that both the desire and ability to attack them scientifically is of the utmost importance. It is the hope of the author that the students of this book will find not only that they have learned about substances and their transformations but will find themselves more inclined as well as able to treat scientifically, all problems, whether chemistry or not, which are appropriate for scientific treatment.

**8. Properties Used to Recognize Substances.** Many substances have characteristics so marked that there is little likelihood of their being confused with other substances. The color of copper distinguishes it from other metals. The elasticity of rubber, the taste of sugar, the odor of ether serve to distinguish these substances, even in the absence of further tests, from others met in ordinary life. We constantly apply such obvious tests as those of color, luster, hardness, odor and taste. We distinguish quite readily between solids, liquids and gases. Very often, however, we need to refine our methods of observation, to make accurate measurements or to use less obvious properties for distinguishing substances. Instead of being content with saying that lead is "heavier" than iron, it is desirable to express this "heaviness," or **density**, numerically by determining the weight of a unit volume, usually **the number of grams per cubic centimeter**. The refractive index of a transparent body can be determined with great exactness and is a most valuable means of identification. Other properties include the coefficient of expansion, the conductivity for heat or

electricity, the boiling point, the melting point, the specific heat, the heat of fusion or of vaporization, surface tension and viscosity.<sup>1</sup>

The chemical changes which substances undergo offer important means of identification. Gold may be indistinguishable in appearance from a certain sample of brass, but nitric acid at once differentiates them by dissolving the latter. Powdered talc and starch in a face powder may readily be differentiated by the fact that the latter will swell up and dissolve in boiling water, or that it will readily burn.

9. The behaviors of substances that involve chemical changes are called their **chemical properties**, while the others are called **physical properties**. This is a distinction which is often insisted upon, but which we should not take too seriously. It is impossible now-a-days to erect any boundary between chemistry and physics nor is it desirable to do so. Both text books and researches in the two sciences show considerable overlapping.

10. **Heterogeneous Mixtures.** As we attempt to apply our tests to distinguish substances, we notice that some materials give a rather ambiguous answer. How shall we state the color, density or hardness of a piece of granite? On close examination we find it composed of several kinds of minerals, having different degrees of hardness, different colors and different properties in general. Although we might determine the density of a given piece of granite, it would be folly to regard this the density of granite in general, because the components of granite are present in different proportion in different samples. Granite is obviously a mixture and not a pure substance, and its properties change abruptly from one small region to another. All of the regions of the same kind together constitute a **phase**. In the case of granite there are three phases: quartz, mica

<sup>1</sup> For definitions of these and other properties see Latimer and Hildebrand, *Reference Book of Inorganic Chemistry*, Macmillan Co., glossary.

and feldspar. The freezing mixture used in making ice cream consists of three phases: all of the pieces of ice together constitute one phase, the crystals of salt another, and the salt solution the third. Some alloys, such as solder, appear quite uniform to the eye, as if they contained but one phase, whereas, by careful etching with acid and using a microscope with reflected light, it is evident that the alloy is heterogeneous, more than one phase being present. **A mixture containing more than one phase is called heterogeneous.**

Evidently, then, the first step in our examination and classification of matter is to separate heterogeneous mixtures into their component homogeneous phases. This may be accomplished by purely mechanical means, which may vary with the nature of the separation. A suspended solid may be removed from a liquid by filtration. A fog (liquid particles) or a smoke (solid particles) may be removed from a gas by the same means. Two solids might be picked apart, though such a process would often be impracticable. Where two kinds of solid particles have different densities it is sometimes possible to employ a liquid whose density is such that one solid will rise to the surface while the other stays on the bottom, as would be the case if a mixture of sand and sawdust were thrown into water. Two liquids which do not mix, such as kerosene and water, are easily separated by skimming or some equivalent process. Where one is emulsified in the other, the highly dispersed globules of the one may often be made to coalesce prior to a separation, as when butter is obtained from cream.

**11. Solutions.** Having separated heterogeneous mixtures into single phases, our next step is the examination of these phases. We will find that a phase may consist of one pure substance, or of two or more substances, in which case it is called a **solution**. For example, we may mix sugar and water, two pure substances, getting a solution, uniform throughout in its properties, in which the sugar can neither

be seen with a microscope nor filtered out. It is not distinguishable from a pure substance in appearance. It can be distinguished, however, by the fact that its properties depend on the relative amounts of its component pure substances. The properties of a pure substance are always the same at the same temperature and pressure. Pure water always has the same density, provided that the pressure and temperature at which the density is measured are kept the same. Ice always melts to water at the same temperature unless a different pressure is applied to it, and even then for every pressure there is a definite melting point. Similarly the boiling point of water depends only upon the barometric pressure. The properties of solutions, on the other hand, depend on the composition, as well as on the temperature and pressure. The properties of a sugar solution are not completely defined by the temperature and pressure alone, as is the case with pure sugar or pure water. In order to predict the density or sweetness of such a solution, or the temperature at which it would freeze or boil, we would have to know its composition, *i.e.*, how much sugar there is in a given amount of water. In general, then, **the properties of a solution depend not only upon the temperature and pressure, but upon the composition as well.**

12. The experimental distinction between a pure substance and a solution is quite simple when the solute (the dissolved substance) is not volatile so that it is left behind when the solvent is evaporated. However, when both are volatile the matter is not quite so simple and it is necessary to find out whether any change in composition and hence in properties occurs during a change in state. By changes in state we understand any change between solid, liquid and gas, such as freezing, boiling, condensation, sublimation, solution or crystallization.

Suppose, for example, we wish to determine whether air is a pure substance or a solution. One method would be to liquify a certain amount and then observe what happens to

it as it slowly evaporates. As the evaporation proceeds one may observe that (a) the light blue color gradually becomes deeper; (b) the temperature of the liquid slowly rises (cf. Fig. 1); (c) the densities of both liquid and gas change; there is a gradually increasing attraction of the liquid by a magnet; (d) different samples of the gas given off show increasing power to support combustion. Any one of these as well as other possible observations show that air must be composed of two or more substances whose properties change during the evaporation causing the observed changes in properties due to differences between the components in color, volatility, density, magnetic susceptibility, chemical behavior. Still other properties might have been used.

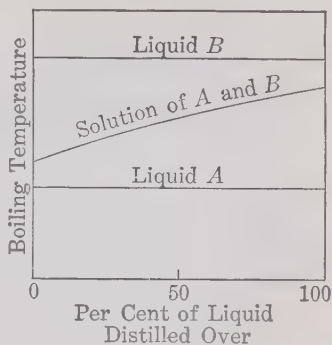


FIG. 1. Experimental distinction between pure liquids and liquid solutions.

13. The term solution is not restricted to liquid solutions, although they furnish the most familiar examples. All gases are completely miscible with each other, forming but one phase, so that every mixture of gases is a solution. Alloys of silver and gold, no matter what the relative amounts of the two metals, contain but one kind of crystal, the properties of which, such as density, color, electrical conductivity, melting point, change continuously with the composition. This is a **solid solution**, and may be contrasted with alloys of copper and silver, which contain two kinds of crystals through a certain range of composition. This could be shown, first, by the microscope; second, by the fact that alloys of these latter metals, though of different composition, would all begin to melt at the same temperature. This is true because a change in the proportion of the metals produces no change in the nature of the two crystals



but simply in their relative amount, and the melting and boiling points of substances never depend upon how much of the substance is used.

**14.** Hardened steel is a solid solution, for though it contains carbon it shows but one kind of crystal under the

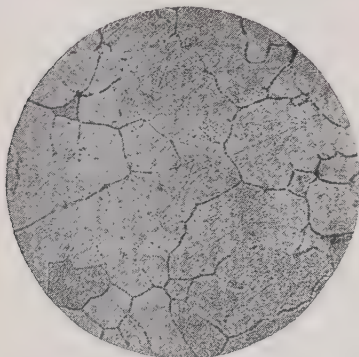


FIG. 2. Hardened steel.

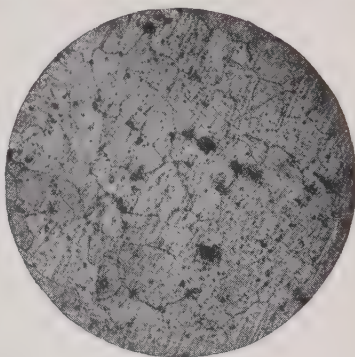


FIG. 3. Wrought iron.

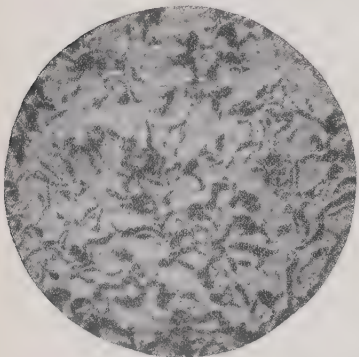


FIG. 4. Gray cast iron.



FIG. 5. Annealed steel.

microscope, as shown in Fig. 2, just as does wrought iron, Fig. 3, which is nearly pure iron. Gray cast iron, however, contains graphite crystals, as shown in Fig. 4, and is obviously heterogeneous, as is annealed steel, Fig. 5, which consists of an intimate mixture of pure iron, of the kind shown in Fig. 3, with an iron carbide.

**15.** If liquid air is distilled in a scientifically constructed



still, it is possible to separate it into two nearly pure constituents, just as water and alcohol can be separated. One of these constituents, **nitrogen**, is found to be slightly lighter than air; it can be condensed to a colorless liquid boiling at  $-194^{\circ}\text{C}.$ ; it is very inert chemically, reacting with but few other substances. The other constituent, **oxygen**, is slightly heavier than air; it gives, when condensed at low temperatures, a blue liquid boiling at  $-182.5^{\circ}\text{C}.$ , and it reacts readily with many substances. Ordinary combustible materials burn in it very vigorously.

16. As another illustration, suppose we have a solid metal which appears perfectly homogeneous under the microscope. We could determine whether it is a solution or a pure substance by melting it, dipping into the melt a suitable thermometer and letting it cool slowly, taking temperature readings at regular intervals, and plotting temperature against time. If the metal is a pure substance we would get a curve like *a*, Fig. 6, but if the metal consists of two components the

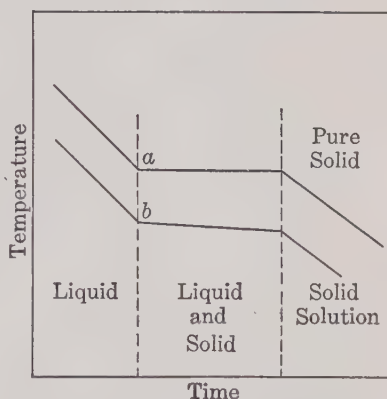


FIG. 6. Experimental distinction between pure solids and solid solutions.

curve would be like *b*, for the solid which freezes out would, in general, have a composition different from that of the liquid and the freezing temperature would alter with the composition.

17. **Compounds and Elements.** Having found out how to separate mixtures into their pure components, let us consider what further we may learn about the composition of pure substances. This question may be answered by means of appropriate chemical reactions. They may consist in producing the substance in question by direct combination

of other substances, a process called **synthesis**, meaning putting together; or we may separate the substance into simpler constituent substances, a process called **analysis**, meaning taking apart. If molten lead is exposed to the air, it becomes coated with a scum, and if this is constantly removed, the lead entirely changes into another substance, called litharge, with a considerable increase in weight, indicating that something has been absorbed from the air. Of the two main constituents of the air only one, the oxygen, will transform the lead in this way. We would conclude from these facts that the litharge is composed of lead and oxygen, or, as chemists would say, is a **compound** of lead and oxygen. This would be the synthesis of litharge.

18. On the other hand, we could put litharge into a crucible, heat it to a red heat, pass over it some illuminating gas, when we would find that it changed into lead, with a loss in weight. Evidently litharge contains lead plus some other constituent which has been removed by the illuminating gas. Further experiments might be performed to prove this other constituent to be oxygen. This would be the analysis of litharge, and from it, likewise, we would conclude that litharge is a compound of lead and oxygen.

19. Again, if we pass an electric current through water, using platinum or gold electrodes to introduce the current into the water, we find that gases are given off at the electrodes and water is used up. If we collect the gas given off at the negative electrode, we find that it is very light, that soap bubbles filled with it rise like balloons, and that it will burn in air with a faintly luminous, very hot flame. This gas is **hydrogen**. The other gas is slightly heavier than air, will not burn in air, but burning substances thrust into it will continue to burn with greatly increased vigor and brilliancy. This gas is oxygen, also one of the constituents of air. From this analysis of water we may conclude that water is a compound of hydrogen and oxygen. The analysis might be made in many other ways. We might also syn-

thesize water by allowing hydrogen and oxygen to combine, which they do very readily.

20. Now it has never been possible to resolve lead, oxygen and hydrogen into simpler substances. These substances, and all others which have never by ordinary chemical reactions<sup>1</sup> been resolved into simpler substances, are called **elements**. Ninety-two are known at the present time. They can form almost endless combinations with each other; considerably over one hundred thousand are known and new ones are constantly being prepared.

The table on page 14 contains a list of the chemical elements. Many of them are well-known substances; many are rare, occurring in but small quantities.

21. **Symbols.** Along with each element in the table is given a characteristic number, whose significance will be explained later, and also a symbol used as an abbreviation of the name. It consists of the initial letter of the name, followed, where necessary to distinguish between several elements having the same initial, by a second appropriate letter. In many cases the symbol follows the Latin name of the element rather than the English name, allowing the symbols to be practically the same in all the principal languages. Thus, the symbol for iron is Fe, from the Latin *ferrum*; that for gold is Au, from the Latin *aurum*, etc.

22. **Classification of the Elements.** The elements may be classified in various ways, any of which might be useful for certain purposes. Some of them are solids, some liquids and some gases, at ordinary temperature and pressure. This is, however, not a very fundamental distinction, as each element may be made to exist in any of these states by suitable alterations in temperature and pressure. The most useful classification is that furnished by the Periodic System, whereby the elements are arranged in families or groups which show similar properties. This arrangement

<sup>1</sup> Certain elements decompose into others by a different type of change called radioactive, to be treated in Chapter XVII.

## THE CHEMICAL ELEMENTS

ELEMENT	SYM- BOL	ATOMIC WEIGHT	ELEMENT	SYM- BOL	ATOMIC WEIGHT
Aluminum . . . .	Al	26.97	Molybdenum . . .	Mo	95.95
Antimony (Stibium)	Sb	121.76	Neodymium . . .	Nd	144.27
Argon . . . . .	A	39.94	Neon . . . . .	Ne	20.183
Arsenic . . . . .	As	74.91	Nickel . . . . .	Ni	58.69
Barium . . . . .	Ba	137.36	Nitrogen . . . .	N	14.008
Beryllium . . . .	Be	9.02	Osmium . . . . .	Os	190.2
Bismuth . . . . .	Bi	209.00	Oxygen . . . . .	O	16.000
Boron . . . . .	B	10.82	Palladium . . . .	Pd	106.7
Bromine . . . . .	Br	79.916	Phosphorus . . .	P	31.02
Cadmium . . . . .	Cd	112.41	Platinum . . . .	Pt	195.23
Calcium . . . . .	Ca	40.08	Potassium		
Carbon . . . . .	C	12.010	(Kalium) . . . .	K	39.10
Cerium . . . . .	Ce	140.13	Praseodymium . .	Pr	140.92
Cesium . . . . .	Cs	132.91	Protoactinium . .	Pa	231
Chlorine . . . . .	Cl	35.457	Radium . . . . .	Ra	226.05
Chromium . . . . .	Cr	52.01	Radon . . . . .	Rn	222
Cobalt . . . . .	Co	58.94	Rhenium . . . . .	Re	186.31
Columbium . . . .	Cb	92.91	Rhodium . . . . .	Rh	102.91
Copper (Cuprum) .	Cu	63.57	Rubidium . . . .	Rb	85.48
Dysprosium . . . .	Dy	162.46	Ruthenium . . . .	Ru	101.7
Erbium . . . . .	Er	167.2	Samarium . . . . .	Sm	150.43
Europium . . . . .	Eu	152.0	Scandium . . . .	Sc	45.10
Fluorine . . . . .	F	19.00	Selenium . . . . .	Se	78.96
Gadolinium . . . .	Gd	156.9	Silicon . . . . .	Si	28.06
Gallium . . . . .	Ga	69.72	Silver (Argentum) .	Ag	107.880
Germanium . . . .	Ge	72.60	Sodium (Natrium)	Na	22.997
Gold (Aurum) . . .	Au	197.2	Strontium . . . .	Sr	87.63
Hafnium . . . . .	Hf	178.6	Sulfur . . . . .	S	32.06
Helium . . . . .	He	4.003	Tantalum . . . . .	Ta	180.88
Holmium . . . . .	Ho	163.5	Tellurium . . . .	Te	127.61
Hydrogen . . . . .	H	1.0081	Terbium . . . . .	Tb	159.2
Illinium . . . . .	Il	?	Thallium . . . . .	Tl	204.39
Indium . . . . .	In	114.8	Thorium . . . . .	Th	232.12
Iodine . . . . .	I	126.92	Thulium . . . . .	Tm	169.4
Iridium . . . . .	Ir	193.1	Tin (Stannum) . .	Sn	118.70
Iron (Ferrum) . . .	Fe	55.84	Titanium . . . . .	Ti	47.90
Krypton . . . . .	Kr	83.7	Tungsten		
Lanthanum . . . . .	La	138.90	(Wolfram) . . . .	W	183.92
Lead (Plumbum) . .	Pb	207.22	Uranium . . . . .	U	238.07
Lithium . . . . .	Li	6.940	Vanadium . . . . .	V	50.95
Lutecium . . . . .	Lu	175.0	Xenon . . . . .	Xe	131.3
Magnesium . . . .	Mg	24.32	Ytterbium . . . .	Yb	173.04
Manganese . . . . .	Mn	54.93	Yttrium . . . . .	Y	88.92
Masurium . . . . .	Ma	?	Zinc . . . . .	Zn	65.38
Mercury			Zirconium . . . .	Zr	91.22
(Hydrargyrum) . .	Hg	200.61			

will be used very extensively later, after we have explained the basis upon which it is made.

One of the most useful divisions is that into metals and non-metals. Several characteristics of metals and non-metals are familiar to all. Metals are characterized by an appearance called metallic luster, by malleability and ductility, and by relatively high conductivity for heat and electricity. These physical differences are accompanied by fundamental differences in chemical behavior to be discussed later.

**23.** From what has just been said it must not be supposed that the metallic state is peculiar to elements. There are many compounds which are metallic also. The further classification of compounds will, however, be deferred to a later chapter, where we shall see that the metallic or non-metallic character of the component elements furnishes a basis for this classification.

This distinction is not rigid, for the two classes shade into each other, as illustrated by carbon, which, in the form of graphite, has some metallic luster and is a fair conductor of electricity, or by arsenic, which has metallic luster but is very brittle. Indeed most of our schemes of classification are arbitrary, purely for our own convenience, and are not due to sharp natural boundaries.

**24. Summary.** The classification of materials that has been presented in this chapter may be summarized in the following table. It is not important to memorize the table, but it is important to understand the nature of the distinctions it indicates.

### **Kinds of Matter:**

**Heterogeneous.** Separable by mechanical means into  
**Homogeneous.**

**Solutions.** Separable by changes of state into

**Pure Substances.**

**Compounds.** Separable by chemical reactions into  
**Elements.**

25. It is to be noted that this classification is based entirely on experimental criteria. It is possible to express it in quite another way, in terms of the structure of matter. Although the concepts of atom and molecule are to be logically developed in the following chapters, most readers are already sufficiently acquainted with them to justify their elementary use here. The foregoing classification may be expressed in these terms as follows:

### Kinds of Matter:

**Heterogeneous.** Different kinds of visible regions separated by sharp boundaries.

**Homogeneous.** Visually uniform throughout.

**Solutions.** Different molecular species irregularly mixed.

**Pure Substances.** Molecules all of one species.

**Compounds.** Different atomic species within the molecules.

**Elements.** Atoms and molecules each of one species.

### EXERCISES

1. Make as large a list as you can of the properties which serve to identify and distinguish substances.

2. What experimental evidence would serve to distinguish (a) a gaseous element from a gaseous compound; (b) a solid solution from a pure substance; (c) whether kerosene is a pure substance?

3. Many years ago the process of combustion was explained as the escape of "phlogiston." Thus metallic magnesium was supposed to give a white ash or "calx," with loss of phlogiston. What evidence could there be to contradict this theory?

4. Classify the following substances according to the above table, giving reasons; where you are not sure of the classification devise an experiment which would enable you to decide: concrete, air, tobacco smoke, well water, paint, glass, fog, salt, copper.

5. Define each of the following terms: phase, element, symbol, metal, substance, solution, property, compound, density, melting point, boiling point, chemical reaction, volatility, crystalline form.

6. Criticize the following definition: "Chemistry is the science which deals with the deep-seated permanent changes in matter."



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## Chapter II

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### *Weight Relations in Chemical Reactions— Atoms and Molecules*

1. An examination of the amounts of material involved is fundamental to an understanding of chemical reactions. The practical importance of this has been referred to already in Chapter I, but we shall soon see that further consideration of these relations gives rise to theories and laws which lie at the very foundations of modern chemical science.

2. **Law of the Conservation of Mass.** Everyday experience teaches us that many changes in matter take place without any change in weight of the materials involved (weight being the usual measure of mass). Thus 100 lb. of ice, on melting, give 100 lb. of water; 1 lb. of salt dissolved in 10 lb. of water gives 11 lb. of solution; the weight of slaked lime equals the weight of quicklime from which it is made plus the weight of the water added in slaking. It is true that there is a loss in weight when quicklime is made from limestone, but that is because a gas, carbon dioxide, is given off, and if this were caught, compressed into a cylinder, as is often done, and weighed, its weight would be found exactly equal to the loss in weight when the limestone changed into quicklime. Similarly, although, when something burns, it may seem to disappear, that is only because gases are formed which escape notice. If a candle is allowed to burn in a closed vessel, no change in weight can be detected.

As a result of vast scientific experience it may be asserted with great confidence that in every chemical reaction the sum of the masses of the products is the same as that of the substances taken. This is known as the **Law of the Conservation of Mass**, or sometimes as the **Indestructibility of Matter**. It has been tested with considerable accuracy in millions of cases, and with extreme accuracy in a number of them, so that there is hardly another scientific law in which we have such confidence.

3. It is violated appreciably only in reactions in which new atoms are formed, involving enormous quantities of energy, in which cases it is the sum of the mass and the energy that is unchanged. However, it takes enormous energy changes to have a detectable influence on mass, for 1 g. is equivalent to  $9 \times 10^{20}$  ergs. To make this relationship more real we may note that if 50 liters of hydrogen measured at 1 atmosphere and room temperature weighing 4.032 grams, were converted entirely into helium, the loss in mass would be 0.03 gram and the energy evolved would be 700,000,000 kilogram calories, enough heat to raise 7000 tons of water from freezing to boiling temperature. This heat is 5,000,000 times the amount that would be liberated in burning this same amount of hydrogen. Conversely, the heat lost in burning hydrogen, which is large as chemical reactions go, corresponds to a change far too small to detect on the most delicate balance.

4. **Law of Simple Multiple Proportions.**<sup>1</sup> When pure substances are analyzed there is frequently found more than one compound of the same elements, the difference being due to the different proportions in which the elements are united. For example, there are three oxides of lead: litharge, used in glazing pottery, red lead, used in certain paints, and lead dioxide, which gives the brown color to the heads of certain kinds of matches, and which forms the

<sup>1</sup> It is customary to consider a "Law of Definite Proportions," but since the identification of the pure substances, to which alone it can be applied, involves constancy of composition, as explained in Chapter I, it should be evident that this "law" is simply the definition of a pure substance, reversed. Experiments to prove this law to the student are always carefully selected so as to avoid solutions, without, however, explaining why such selection is necessary. An adequate definition of chemical compounds, including their differentiation from solutions, makes the law of definite proportions a superfluity.

positive plate of a lead storage battery. The proportions of lead to oxygen in these three compounds are found by analysis to be as follows: litharge, 1 to 0.0772; red lead, 1 to 0.1029 ( $= \frac{4}{3} \times 0.0772$ ); lead dioxide, 1 to 0.1544 ( $= 2 \times 0.0772$ ). It is to be noted that the proportions of oxygen in the red lead and lead dioxide are simple multiples of that in litharge,  $\frac{4}{3}$  and 2, respectively.

Again, in addition to water, we know of another compound of hydrogen and oxygen, hydrogen peroxide, a solution of which in water is found in most medicine closets for use as an antiseptic, cleansing or bleaching agent. This substance is unstable, and readily gives up half of the oxygen it contains, leaving water. The relative amounts of hydrogen and oxygen in water and in hydrogen peroxide are as follows: water, 1 to 7.94; hydrogen peroxide, 1 to 15.88. In proportion to the hydrogen there is just twice as much oxygen in the second compound as in the first. An almost endless number of illustrations of this nature might be given, and we would find that whenever the same elements form more than one compound, if the weights are in the ratio  $a$  to  $b$  in one they will be in some simple multiple of this in another, such as  $a$  to  $2b$ ,  $a$  to  $3b$ ,  $2a$  to  $3b$ ,  $3a$  to  $4b$ . The same simplicity is apparent when more than two elements combine to form different compounds. This experience is summarized in the **Law of Simple Multiple Proportions**, which may be stated as follows: **Whenever the same elements form more than one compound, their proportions in the different compounds are simple multiples of each other.**

**5. The Atomic Theory.** The existence of the law of simple multiple proportions suggests the question, What fundamental quality of matter is responsible for this behavior? This state of affairs could evidently be true only if each chemical element is composed of minute particles, which we call **atoms**, all alike for the same element, and compounds are formed by simple combinations of different kinds of atoms. For example, one atom of element A, hav-

ing weight  $a$ , might combine with one atom of element B, having weight  $b$ , to form a particle of a compound AB. It is obvious that no matter how many of these particles we take, the ratio of the weights of the elements in the compound would be  $a$  to  $b$ . The same elements might also form a different compound by a different combination of atoms, such as by one atom of A combining with two atoms of B, to form a particle which may be designated by  $AB_2$ . Evidently the ratio of weights of the elements A and B in a particle of this compound, and hence in any number of particles, would be  $a$  to  $2b$ . There is here twice as much of element B with respect to A in the second compound,  $AB_2$ , as in the first, AB, in accordance with the experience summarized in the law of simple multiple proportions. If still other compounds of A and B are formed, we would expect other simple combinations of atoms, such as  $A_2B$ ,  $AB_3$ ,  $A_2B_3$ ,  $A_3B_2$ . Accordingly, if the ratio of the weights of A and B in one compound is  $a/b$ , we would expect to find in another compound some such ratio as  $2a/b$ ,  $a/3b$ ,  $2a/3b$ ,  $3a/2b$ .

There are two ways in which we may imagine matter to be constituted; either it is continuous, as it appears to the eye, so that we might go on subdividing it indefinitely and never reach any portion, however small, that could not be still further subdivided without losing its identity, or else matter may have a granular structure, so that when we have subdivided it until these ultimate grains are reached, no further subdivision is possible without fundamentally altering the nature of the material. That the latter assumption corresponds to the facts is indicated by the Law of Simple Multiple Proportions. If we add to this the evidence furnished by the kinetic theory of gases, by radioactive phenomena and colloids, to be discussed in later chapters, we may conclude that the atomic structure of matter is more than a mere theory, and rather an established fact. We owe this atomic theory of matter chiefly to the English school-master-chemist, John Dalton.

6. The smallest group of atoms that can exist isolated from other like groups, as in a gas or in solution, is called a molecule. The molecule of a compound contains more than one kind of atom. The molecule of an element consists of one or more like atoms. The atoms of the elements are designated by the symbols given in the table on page 14. For example, H denotes an atom of hydrogen. In hydrogen gas, a pair of atoms forms a molecule, designated  $H_2$ . Similarly the oxygen atom is O and the molecule is  $O_2$ . A molecule of water is designated by the **formula**,  $H_2O$ , indicating that it contains two atoms of hydrogen and one atom of oxygen. The evidence for these formulas will be presented later, our purpose at present being merely to explain the significance of chemical symbols and formulas.

7. **Numerical Values of Atomic Weights.** The actual weights of the atoms are exceedingly small, expressed in ordinary units, such as grams,<sup>1</sup> and it is far more convenient to select a much smaller weight as unit, such as the weight of one of the atoms themselves. It is purely arbitrary which atom we choose and what number we assign to it, so long as we select corresponding values for the other atoms. Thus, knowing that the molecule of water contains 8 times as much oxygen as hydrogen, and granting that  $H_2O$  is the correct formula for it, we might call  $O = 100$ , when H would be 6.25; or again, if we let  $O = 1$ , then  $H = 0.0625$ , etc.

The choice appeared a very simple one to most early chemists, who, finding that the atom of hydrogen is lighter than that of any other known element, decided to call its weight 1, corresponding to atomic weights greater than one for all other elements. Later it was found that the ratio of weights of the atoms of hydrogen and oxygen is not exactly 1 to 16, but 1 to 15.88, and that if we take  $O = 16$  as our unit, making  $H = 1.008$ , the atomic weights of most of the other elements come out much nearer whole numbers

<sup>1</sup> It would take approximately  $6 \times 10^{23}$  atoms of hydrogen to weigh 1 g.



than if we let  $H = 1$  and  $O = 15.88$ . This is illustrated by the following sets of values based on the two assumptions.

Hydrogen . . . . .	<b>1.008</b>	<b>1.000</b>
Oxygen . . . . .	<b>16.00</b>	<b>15.88</b>
Calcium . . . . .	40.07	39.67
Carbon . . . . .	12.00	11.91
Lithium . . . . .	6.94	6.89
Magnesium . . . . .	24.32	24.13
Nitrogen . . . . .	14.01	13.90
Phosphorus . . . . .	31.03	30.82
Potassium . . . . .	39.10	38.80
Sodium . . . . .	23.00	22.83
Sulfur . . . . .	32.06	31.82

An additional reason for the choice of  $O = 16.00$  lies in the fact that but few of the elements form compounds with hydrogen, while nearly all form compounds with oxygen, and hence the atomic weight ratio between an element and oxygen can be determined directly, while the atomic weight ratio between the element and hydrogen could only be determined indirectly, and would therefore be subject to greater error.

8. The numerical values of the atomic weights permit us to extend the meanings of chemical formulas to include the relative weights of the elements contained in compounds. For example, the formula,  $CO_2$ , indicates not only a molecule of carbon dioxide, composed of one atom of carbon and two atoms of oxygen, but since an atom of carbon weighs 12, if the weight of an atom of oxygen is called 16, the molecule weighs 44 and contains 12 parts by weight of carbon and 32 parts by weight of oxygen. Furthermore, since this proportion,  $\frac{\text{wt. C}}{\text{wt. O}} = \frac{12}{32}$ , applies to any molecule, it applies to any number of molecules and to any units of weight. Hence we can write for  $CO_2$ ,

$$\frac{\text{wt. C}}{\text{wt. O}} = \frac{12 \text{ atomic wt. units}}{32 \text{ atomic wt. units}} = \frac{12 \text{ g.}}{32 \text{ g.}} = \frac{12 \text{ lb.}}{32 \text{ lb.}} = \frac{12 \text{ oz.}}{32 \text{ oz.}} \\ = \frac{1.000 \text{ g.}}{2.667 \text{ g.}}, \text{ etc.}$$



**9. Gram-atoms and Gram-molecules, or Moles.** Although we reason in terms of atoms and molecules, we work with vastly larger amounts of material, and it is often convenient to give a somewhat different meaning to symbols and formulas so as to express relative weights in units actually used.

If  $6 \times 10^{23}$  atoms of any element are used, their weight in grams is numerically equal to the atomic weight. This amount of an element is called a gram-atom. Thus 12 g. of carbon is 1 gram-atom of carbon, 16 g. of oxygen is 1 gram-atom of oxygen.

Similarly,  $6 \times 10^{23}$  molecules are a gram-molecule or mole, whose weight in grams is numerically equal to the molecular weight. Thus 44 g. of  $\text{CO}_2$  is 1 mole of  $\text{CO}_2$ . A symbol thus has a double meaning, standing (a) for 1 atom, or (b) for 1 gram-atom. A formula, similarly, stands for (a) 1 molecule, or (b) 1 mole. This double meaning may seem at first a little confusing, but experience shows the difficulty to be trivial.

It is evident that, given the weight ratio implied by a formula, it is possible to calculate any other. Suppose, for example, we wished to calculate what weight of lead, Pb, could be obtained from 100 g. of  $\text{Pb}_3\text{O}_4$ . We see that 1 molecule of  $\text{Pb}_3\text{O}_4$  could yield 3 atoms of Pb, therefore 1 mole of  $\text{Pb}_3\text{O}_4$  could yield 3 gram-atoms of Pb. Since 1 gram-atom of Pb is 207 g. (cf. p. 14) and 1 gram-atom of O is 16 g., 1 mole of  $\text{Pb}_3\text{O}_4$  weighs 685 g. and contains 621 g. of Pb. Hence 1 g. of  $\text{Pb}_3\text{O}_4$  contains  $621 \div 685$  g. of Pb and 100 g. of  $\text{Pb}_3\text{O}_4$  contains  $100 \times 621 \div 685$  or 90.7 g. of Pb.

**10.** In stating the problem in this way we are using the concept of the proportionality of  $\text{Pb}_3\text{O}_4$  to Pb. The author regards such a separation into logical steps, each of which can be scrutinized, as preferable to the formal proportion,  $685 : 621 :: 100 : x$ , which is so often used by teachers of chemistry. It is too easy to get the figures in the wrong

places, too hard to check an error, and the rule for solving the proportion too often seems like something quite apart from ordinary algebraic procedure. If a more formal statement than the above is preferred it is suggested that the following be written:

$$\frac{\text{wt. Pb}_3\text{O}_4}{\text{wt. Pb}} = \frac{(3 \times 207) + (4 \times 16) \text{ g.}}{3 \times 207 \text{ g.}} = \frac{100 \text{ g.}}{x}$$

The two numerical ratios thus equated can be easily verified and can be solved by the ordinary algebraic method.

**11. Chemical Equations.** When a chemical reaction takes place there is a rearrangement of atoms into new groups, or molecules, forming new substances. This is indicated by a **chemical equation**, in which the rearrangement is shown by the regrouping of the atomic symbols to represent the new molecular species formed. For example, the formation of iron and carbon dioxide,  $\text{CO}_2$ , from the ore  $\text{Fe}_2\text{O}_3$  by the action of carbon monoxide,  $\text{CO}$ , is represented by the equation



The following facts may be noted about such an equation:

First, an equation tells nothing about the conditions necessary for carrying out the reaction, and the mere writing of an equation does not imply that the reaction it represents can actually be realized.

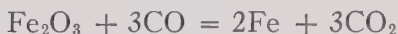
Second, it must represent the fact that no matter disappears, by showing the same number of atoms of each element on both sides of the equation, though they are arranged in different molecules.

Third, it represents the relative number of molecules of each substance taking part in the reaction.

Fourth, it represents the relative weights of each substance, which can be readily computed with the aid of the table of atomic weights.

The above equation, then, may be read as follows: 1 molecule of ferric oxide reacts with 3 molecules of carbon monoxide to yield 2 molecules (or atoms) of iron and 3 molecules of carbon dioxide; also,  $2 \times 56 + 3 \times 16$  parts (by weight) of iron oxide react with  $3(12 + 16)$  parts of carbon monoxide to give  $2 \times 56$  parts of iron and  $3(12 + 32)$  parts of carbon dioxide. These parts by weight may be in any kind of weight unit, pounds, tons, ounces, grams, etc. In accordance with our double usage of the symbols and formulas to represent not only single atoms and molecules, but also gram-atoms and gram-molecules, or moles, as explained on page 23, we often read an equation in terms of grams; hence,  $160 \frac{160}{g.}$  of iron oxide, when reacting with 84 g. of carbon monoxide, give 112 g. of iron and 132 g. of carbon dioxide, which quantities represent 1 mole, 3 moles, 2 moles and 3 moles respectively.

This may be summarized briefly by writing under each formula in the equation its complete meaning in both of the above senses.



(1) Number of molecules	1	3	2	3
Weight, in terms of one sixteenth the weight of an oxy- gen atom . . .	160	84	112	132
(2) Number of moles .	1	3	2	3
Weight . . . .	160 g.	84 g.	112 g.	132 g.

**12. Calculation of Weight Relations.** The meaning thus attached to chemical formulas and equations makes it possible to calculate the weights of all the other substances involved in a chemical reaction from the weight given for any one of them. Suppose, for example, that it is required to find the weight of iron that should be obtained from 100 lb. of the oxide of iron considered above. From the

112  
98  
160

112  
98  
160

weights implied by the formulas, as explained above, we may write the following:

160 g. of  $\text{Fe}_2\text{O}_3$  gives 112 g. of Fe.

160 lb. of  $\text{Fe}_2\text{O}_3$  gives 112 lb. of Fe.

1 lb. of  $\text{Fe}_2\text{O}_3$  gives  $\frac{112}{160}$  lb. of Fe.

100 lb. of  $\text{Fe}_2\text{O}_3$  gives  $\frac{100 \times 112}{160} = 70$  lb. of Fe.

Again, suppose we wish to find the amount of coke, containing 80 per cent carbon, the rest being ash, that is required to reduce to iron the above amount of ore. From the weights implied in the equation, we can say that

1 mole  $\text{Fe}_2\text{O}_3$  requires 3 moles CO, which requires 3 gram-atoms of C.

160 lb.  $\text{Fe}_2\text{O}_3$  requires 36 lb. C.

100 lb.  $\text{Fe}_2\text{O}_3$  requires  $\frac{100}{160} \times 36 = 22.5$  lb. C.

22.5 lb. C is 80 per cent or  $\frac{80}{100}$  of the coke required, which

is  $\frac{100}{80} \times 22.5$  lb. = 28.1 lb.

This connection between atomic weights, formulas and relative weights of substances may be used not only to calculate the relative weights from the formulas and atomic weights, as above, but also to calculate the atomic weights when the formulas and suitable weight relations are known, or again, to determine formulas when the other two factors are known.

**13. Calculation of Atomic Weights.** As an example of the calculation of atomic weights let us suppose that we know the formula of a certain oxide of copper to be  $\text{Cu}_2\text{O}$  and find on analysis that 0.5120 g. of it contains 0.4548 g. of copper, and wish to calculate the atomic weight of copper,

provisionally called  $x$ . We may arrange the steps in the reasoning as follows:

Given by formula	$\text{Cu}_2\text{O}$ contains $2\text{Cu}$ and $0$		
Given weights, by analysis . . . . .	$0.512 \text{ g.}$	$- \quad 0.4548 \text{ g.}$	$= 0.0572 \text{ g.}$
Given relative no. gram-atoms from formula . .		$2$	$1$
Wts. in 1 mole of $\text{Cu}_2\text{O}$ from formula . . . . .		$2x \text{ g.}$	$16 \text{ g.}$
Wts. in 1 mole of $\text{Cu}_2\text{O}$ from analysis . . . . .		$\frac{16}{0.0572} \times 0.4548 \text{ g.}$	$16 \text{ g.}$

Comparing the last two figures in the column for copper both represent the copper combined with 16 g. of oxygen,

hence they are equal, and  $2x = \frac{16}{0.0572} \times 0.4548 \text{ g.}$ , or

$x = 63.6 \text{ g.}$ , hence the atomic weight of copper is 63.6.

**14. Calculation of Formulas.** The third case consists in calculating the formula when the other two factors, atomic weight and composition, are known. Suppose that we find on analysis that a certain chloride of arsenic contains 58.68 per cent of chlorine, and know the atomic weight of arsenic,  $\text{As} = 75.0$ , and chlorine,  $\text{Cl} = 35.5$ , and wish to determine the formula of the compound. Now the formula indicates primarily the relative number of atoms, or of gram-atoms, in the molecule, or mole, respectively, so that we may proceed to determine the number of gram-atoms of one element combined with 1 gram-atom of the other.

Given,

58.68 g. Cl combine with 41.32 g. As

therefore

35.5 g. Cl combine with  $\frac{35.5}{58.68} \times 41.32 = 25.0$  g. As

or,

1 gram-atom Cl combine with  $\frac{25.0}{75.0} = \frac{1}{3}$  gram-atom As

or,

3 gram-atoms Cl combine with 1 gram-atom As

and,

3 atoms Cl combine with 1 atom As,

therefore formula is  $\text{AsCl}_3$ .

### EXERCISES

1. What do you understand by the law of simple multiple proportions?
2. How does the atomic theory explain this law?
3. Write out in words all that the following formulas mean to you:  $\text{H}_2\text{O}$ ;  $\text{H}_2\text{O}_2$ ;  $\text{Ca}(\text{OH})_2$ ;  $\text{FeSO}_4$ .
4. Define symbol, formula, chemical reaction, chemical equation, mole, molecule, atom.
5. How many atoms of oxygen are in 1 molecule of  $\text{Ca}(\text{OH})_2$ ? *Ans.* 2.
6. How many gram-atoms of lead (Pb) are in 2 moles of  $\text{Pb}_3\text{O}_4$ ?  
*Ans.* 6.
7. How many gram-atoms of oxygen would be used up in converting 1 gram-atom of lead into  $\text{Pb}_3\text{O}_4$ ? *Ans.*  $\frac{4}{3}$ .
8.  $\text{PbO}_2$  can be made from  $\text{Pb}_3\text{O}_4$  by the reaction:



How many pounds of  $\text{PbO}_2$  could be obtained from 100 lb. of  $\text{Pb}_3\text{O}_4$ ?

*Ans.* 34.9 lb.

9. How many gram-atoms of sulfur are there in 196 g. of sulfuric acid,  $\text{H}_2\text{SO}_4$ ? *Ans.* 2.

10. What weight of water could be obtained from 1.00 g. of  $\text{Cu}_2\text{O}$ ?

*Ans.* 0.126.

11. How much water would be required to convert 100 g. of phosphorus pentoxide,  $\text{P}_2\text{O}_5$ , into phosphoric acid, the equation being:  $3\text{H}_2\text{O} + \text{P}_2\text{O}_5 = 2\text{H}_3\text{PO}_4$ ? *Ans.* 38 g.

12. What per cent of  $\text{Al}_2\text{O}_3$  is aluminum? *Ans.* 53%.

13. What weight of aluminum, Al, must be used per kilogram of iron oxide,  $\text{Fe}_3\text{O}_4$ , to carry out the reaction:  $8\text{Al} + 3\text{Fe}_3\text{O}_4 = 4\text{Al}_2\text{O}_3 + 9\text{Fe}$ ?

*Ans.* 0.31 kg.



14. When treated with hydrochloric acid, barium peroxide yields hydrogen peroxide according to the following equation:  $\text{BaO}_2 + 2\text{HCl} = \text{H}_2\text{O}_2 + \text{BaCl}_2$ . How much  $\text{BaO}_2$  is required to make 10 lb. of a 5 per cent solution of  $\text{H}_2\text{O}_2$ ? *Ans.* 2.49 lb.

15. What weight of aluminum could be dissolved by 196 g. of sulfuric acid,  $\text{H}_2\text{SO}_4$ ? The equation is:  $2\text{Al} + 3\text{H}_2\text{SO}_4 = \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2$ . *Ans.* 36 g.

16. What weight of  $\text{Fe}_2\text{O}_3$  would result upon burning 10 kilograms of  $\text{FeS}_2$ ? The equation for the reaction is:  $4\text{FeS}_2 + 11\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$ . *Ans.*  $6\frac{2}{3}$  kg.

17. A certain compound of sulfur and oxygen only was found by analysis to contain 2.00 g. of sulfur and 3.00 g. of oxygen. (a) How many grams of oxygen, (b) how many gram-atoms of oxygen would be combined with one gram-atom of sulfur in this compound?

*Ans.* (a) 48.0 g.; (b) 3 g.-atoms.

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# Chapter III

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## *The Kinetic Theory*

1. While we are discussing the general properties of substances it will be profitable to consider certain properties of gases, on account of the existence of important uniformities in their behavior from which we can learn much about molecules. When solids and liquids are heated, they expand, in nearly all cases, but the rate of expansion with the temperature is a specific property of each substance. The same holds true for the compressibility of solids and liquids. With gases, however, the effect of changing temperature or pressure is nearly independent of the particular gas used. This is illustrated by the accompanying table.

TABLE 1

INCREASE IN VOLUME WHEN 1 CUBIC CENTIMETER OF MATERIAL AT 0° C. IS HEATED TO 1° C.

GASES		LIQUIDS	
Acetylene . . . . .	0.003,77	Alcohol . . . . .	0.001,05
Ammonia . . . . .	.003,75	Chloroform . . . .	.001,21
Argon . . . . .	.003,68	Ether . . . . .	.001,56
Carbon monoxide . . . .	.003,67	Mercury . . . . .	.000,18
Chlorine . . . . .	.003,90	Water . . . . .	— .000,06
Helium . . . . .	.003,66	SOLIDS	
Hydrogen . . . . .	.003,66	Common salt . . . .	.000,032
Methane . . . . .	.003,68	Copper . . . . .	.000,017
Oxygen . . . . .	.003,66	Diamond . . . . .	.000,000,27

Similar regularity with gases is evident on examining the compressibility, *i.e.*, the relative decrease in volume on applying pressure.

A further distinction between gases, on one hand, and liquids and solids, on the other, is their tendency to expand indefinitely, so as to fill completely any space at their disposal, always exerting pressure on the walls of the containing vessel.

Again, the rate of diffusion of one gas through another is vastly more rapid than diffusion through a liquid or through a solid, in which case, indeed, measurable diffusion is very rare, as illustrated by sharp boundaries in rocks between minerals which have been in contact for millions of years.

2. Now these characteristics of gases are such as to excite the curiosity of persons having the scientific attitude as to *why* gases behave as they do. We may also wish to be in a position to predict more accurately than we can from the above meager information *how* they behave. The former question is theoretical, the latter immediately practical. We may choose to begin by speculating regarding the answer to the former, or by performing a series of careful experiments to reveal the latter. The former course should yield a theory, the latter the "gas laws." Science advances by using either avenue of approach, now the one, now the other, or both together.

3. The student might, at this point, go into the laboratory and work out by well-controlled experiments the relations between pressure, volume, temperature, mass and molecular weight of one gas; satisfy himself that the formulas obtained are applicable to a number of gases and hence, probably, to all gases. This approach is often called **induction**; it starts with particular cases and leads up to general laws which are essentially descriptions of behavior. The other approach is to construct some theory, model or picture, of the possible structure of gases in this case, from which the behavior of individual gases could be inferred by **deduction**. All the various consequences of the theory should, of course, be tested by experiment before it should be given any great scientific standing.

4. In the present case, the latter approach will be emphasized because the resulting theory is a powerful tool for dealing with other more complicated matters, such as the control of chemical reactions. If it were merely a question of gas behavior, we might leave the whole matter to the physicists, but the theory is of such value to chemists, and so illuminating, indeed, to anyone interested in his physical environment that practice in working it into one's active imagination is rather sure to be rewarding. It is, at least, a labor saver, for it leads so obviously to the correct arithmetical treatment of gas problems as to make it unnecessary to commit to memory formulas almost certain to be misapplied or forgotten.

5. Let us ask the question, what sort of structure must a gas possess in order to account for the above phenomena? The most satisfactory picture is that furnished by the **Kinetic Theory**, which assumes that a gas is composed of particles called **molecules**, whose size is very small compared with the distance between them, and that each molecule is in rapid motion, colliding with other molecules and with the walls of the containing vessel.<sup>1</sup> It is these impacts which produce the observed pressure, a series of rapid impacts obviously having the effect of a steady pressure. The further assumption is made that the average velocity of the molecules, and hence the pressure produced upon the walls of the vessel, depends upon the temperature, increasing as the latter increases. The molecules are in such rapid motion, and are most of the time so far apart, relatively, that their mutual attractions have very little effect.

This picture of the condition of gases has proved to be of such immense service in explaining and predicting their

<sup>1</sup> An idea of the actual values calculated may be obtained from the following figures for oxygen. At one atmosphere pressure and 0° C., one cubic centimeter of oxygen contains  $27 \times 10^{18}$  molecules, moving with an average velocity of 0.46 kilometer per second (about  $\frac{1}{3}$  mile per second). Each molecule travels on an average about 1000 times its own diameter before colliding with another molecule.

properties that it is hardly questioned by scientists at the present time.

**6. Relation between Quantity and Pressure When Volume and Temperature Are Constant.** Let us see first, how, on the basis of the theory just given, we should expect changes in the amount of a gas to be related numerically to changes in pressure. Imagine a gas inclosed in a vessel provided with a cock, as represented in Fig. 1*a*. The vessel is supposed to be immersed in a bath to preserve constant temperature. Let us have very few molecules in the vessel, and visualize them by the dots in the figure. These molecules will all

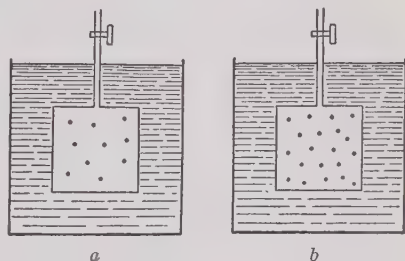


FIG. 1.

be in rapid rectilinear motion, some moving faster, some more slowly, between impacts, but with a certain average velocity depending on the temperature, producing a definite pressure on the vessel walls as they rebound from them. Suppose, now, that we introduce an equal number of the same kind of molecules through the valve, producing the condition illustrated in Fig. 1*b*. It is obvious that since the volume of the vessel remains the same, and the average speed of the molecules is kept the same by the action of the bath in maintaining constant temperature, the only effect of the doubling of the amount of gas is merely to double the number of impacts in a given time per unit of area of the vessel walls, and hence to double the pressure. Evidently we would expect any change in the number of molecules in the vessel to produce a proportional change in the pressure, and since the number of molecules depends on the amount of the gas, we can make the general deduction that **when temperature and volume are kept constant the pressure of a gas is proportional to the amount present.**

As an example of how this may be applied let us consider a tank, with an attached pressure gauge, containing any gas. Allow the gas to escape until the pressure falls from 100 lb. per square inch to 30 lb. It is evident, since the pressure has fallen to 0.3 of its initial value, that there remains in the tank only 0.3 of the gas originally present.

**7. Relation between Pressure and Volume When Temperature and Amount Are Constant.** Let us imagine, next, that the gas is contained in a cylinder like that of a steam

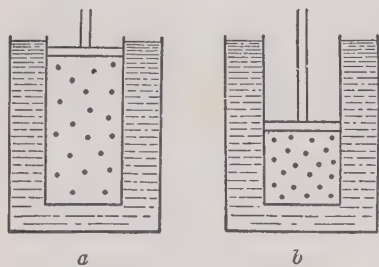


FIG. 2.

engine, with a movable piston, as in Fig. 2, so that the volume of the inclosed gas may be altered without changing the amount. If, now, the piston is pushed down from the position represented by *a*, in the figure, to that represented by *b*, where the volume is half as

great, the number of impacts on a given area of the walls in a given time will be doubled. While the piston is being pushed down, the molecules striking it will rebound a little faster than before, causing a slight increase in temperature,<sup>1</sup> so that we must wait a moment till this temperature has been lowered to that of the bath surrounding the cylinder, when the average speed of the molecules will be the same as before the piston was pushed down. Since the number of impacts on a given area of the walls has been doubled, the pressure is likewise twice what it was before the piston was moved. Evidently, if the volume were made one third as great as at first, the pressure would become three times as great, etc., so that we may conclude in general that **when the temperature and amount of gas are constant the pres-**

<sup>1</sup> This effect may be noticed in the heating of the pump when a bicycle or automobile tire is pumped up.



sure is **inversely proportional to the volume**. This is usually called Boyle's Law.

As an example, let us calculate the final volume when 10 l. of gas at a pressure of 76 cm. of mercury is subjected to a pressure of 19 cm. Since the pressure is **decreased** in the ratio nineteen seventy-sixths, the volume will be **increased** in the same ratio, becoming seventy-six ninetieths of 10 l., the original volume, or 40 l.

**8. Relation between Pressure and Concentration When Temperature Is Constant.** The ratio of the amount of material to the volume in which it is contained, or the amount in unit volume, is called its **concentration**. Evidently it is the concentration which determines the number of impacts, and hence the pressure, so long as the speed of the molecules is unaltered. If, for example, 2 g. of a certain gas in 5 l. exerted a pressure of 2 atmospheres, then 1 g. of the same gas at the same temperature in a volume of 10 l. would be only one fourth as concentrated, and would exert only one fourth of the pressure, which would be one half atmosphere. In general, we may say that **the pressure of a gas is proportional to its concentration when the temperature is constant**.

**9. Relation between the Pressure, Mass and Speed of the Molecules.** Although, as has been said, the pressure exerted by a gas depends upon the velocity of its molecules, it is not directly proportional to the speed, for if the speed is doubled, not only does each molecule hit the vessel walls twice as often, but also twice as hard, for the momentum of each molecule is doubled by doubling the speed. The pressure is thus proportional to the square of the average velocity of the molecules, and hence is proportional to their mean kinetic energy. Moreover, the momentum of each impact is proportional to the mass of the molecules. A heavy molecule would exert more pressure than would a light one moving at the same speed. In a mixture of gases the different kinds of molecules must all have the same kinetic energy,

hence light molecules, like those of hydrogen, must move much faster than heavier ones, like those of oxygen.

### 10. Effect of Temperature, When Amount Is Constant.

Let us next see how a gas would be affected by a change in the temperature. It will be simplest, first, to consider the

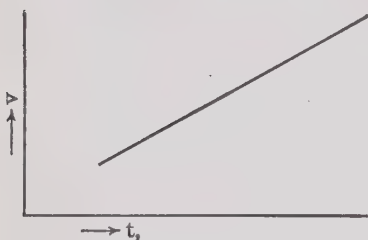


FIG. 3.

effect of this change upon the pressure and volume separately, keeping one constant while the other is allowed to vary. We will imagine a constant weight on the piston of the cylinder containing the gas, so that the volume may vary while the pressure re-

mains the same. We may now vary the temperature by altering that of the bath in which the cylinder is immersed. If the temperature of the gas is increased, we would expect, in terms of our theory, that the molecules would gain in kinetic energy, moving faster and hitting the vessel walls and the piston both harder and more frequently, forcing the latter upwards until the reduction in the number of impacts in a given time compensates for the greater force of each impact. It is found by experiment that this increase in volume is uniform, as expressed by the plot in Fig. 3.

### 11. Absolute Zero of Temperature.

Similarly, if the piston is not permitted to move, so that the volume remains constant, an in-

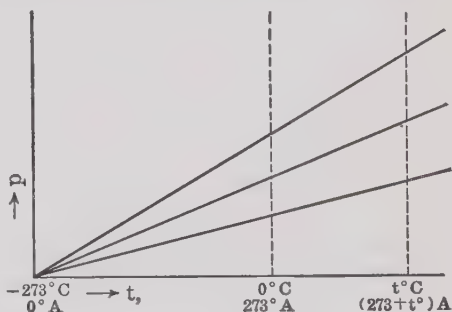


FIG. 4.

crease in temperature would be expected to increase the kinetic energy of the molecules, resulting in harder and more frequent impacts, and hence an increase in pres-

sure. It is found that the increase in pressure with temperature is uniform, as expressed by the plot in Fig. 4, similar to the previous case. By careful measurements the increase is found to amount to  $\frac{1}{273}$  of the value of the pressure at  $0^\circ \text{C}$ . We are led naturally to inquire the effect of a continued **decrease** in temperature. Diminishing the pressure  $\frac{1}{273}$  of its value at  $0^\circ \text{C}$ . for every degree the temperature is lowered would give no pressure at all at  $-273^\circ \text{C}$ . (more exactly,  $-273.15^\circ \text{C}$ .).

What does this mean in terms of the kinetic theory? Since we have attributed gas pressure to the impacts of gas molecules moving with an energy depending on the temperature, when the pressure becomes zero we must conclude that the molecules are no longer in motion, and that we have reached the **Absolute Zero** of temperature. A lower temperature is inconceivable in terms of our theory. This remarkable conclusion is confirmed by the behavior of other properties, many of which approach either zero or infinity, as the temperature approaches  $-273^\circ \text{C}$ .

It is both logical, therefore, and for many scientific purposes more convenient, to reckon temperature from the absolute zero, which is  $273^\circ$  below the centigrade zero. We denote absolute temperature by  $A$ , or by  $K$  for Lord Kelvin. On this scale the melting point of ice,  $0^\circ \text{C}$ ., is  $+273^\circ \text{A}$ .;  $17^\circ \text{C}$ . is  $273 + 17$ , or  $290^\circ \text{A}$ ., and in general, letting  $T$  and  $t$  stand for temperature on the absolute and centigrade scales respectively,  $T = t + 273$ . The most convenient way of expressing the effect of temperature on the pressure is to say that **when the amount and volume of a gas are kept constant, the pressure is proportional to the absolute temperature**, since both depend upon the kinetic energy of the molecules.

**12.** As an example, let us find the final pressure produced when a tank of gas under a pressure of 10 atmospheres is cooled from  $40^\circ \text{C}$ . to  $18^\circ \text{C}$ .  $40^\circ \text{C}$ . is  $313^\circ \text{A}$ ., and  $18^\circ \text{C}$ . is  $291^\circ \text{A}$ . Since the absolute temperature has been lowered

to  $\frac{291}{313}$  of its initial value, the kinetic energy of the molecules will be lowered to  $\frac{291}{313}$  of its initial value, and hence the pressure will be lowered to the same fraction of its initial value, which is  $\frac{291}{313}$  of 10 atmospheres, or 9.3 atmospheres.

When the amount of gas and the pressure are kept constant, any change in the absolute temperature, with its proportionate change in the kinetic energy of the molecules, must be compensated by a proportionate change in volume.

Suppose, for example, that we have 250 cc. of gas at  $27^{\circ}\text{C.}$ , and wish to determine at what temperature the volume will become 200 cc. The new volume will be  $\frac{200}{250}$ , or 0.8 of the old volume; hence the **absolute** temperature will be reduced to 0.8 of its initial value, or from  $300^{\circ}\text{A.}$  to  $240^{\circ}\text{A.}$ , which is  $-33^{\circ}\text{C.}$

**13. Effect of Changing Both Temperature and Pressure, When Amount of Gas Is Constant.** When any two of the factors pressure, temperature and volume are changed, the effect on the third can be calculated by separating the process into two steps similar to the above. For example, suppose we have 50.0 cc. of gas at 74 cm. pressure and  $20^{\circ}\text{C.}$ , and wish to know the volume it would occupy under **standard conditions**, which are **1 atmosphere (76 cm. of mercury) and  $0^{\circ}\text{C.}$**  If we first change the pressure to the final value, since the pressure is increased, the volume will be diminished to  $\frac{74}{76}$  of 50.0 cc. Next, keeping the pressure constant, let us change the temperature from  $20^{\circ}\text{C.}$ , which is  $293^{\circ}\text{A.}$ , to  $0^{\circ}\text{C.}$ , or  $273^{\circ}\text{A.}$  This will cause a further diminution in volume in the ratio  $\frac{273}{293}$ , so that the result of both changes is  $\frac{273}{293} \times \frac{74}{76} \times 50.0$  cc., or 45.3 cc.

**14.** The several gas laws which we have just deduced from the kinetic theory, and which are found to be in accord with experiment, may be expressed by algebraic equations, and may be combined into one fundamental general equation. When one has to apply the gas laws frequently, it is wise to use equations, as the mathematical expression

of a law makes it easier to use. As has been said, "mathematics is a substitute for thought"; it enables one to represent briefly the result of thought, so that the process may be repeated in the future without repeating the reasoning. When, however, the formula is used without the previous thought process, as when it is copied out of a text book, there is the danger that it will be misapplied or forgotten, and even when applied correctly the process is nearly devoid of educational value. Instead of depending on the memory to retain several algebraic equations, we may use the kinetic theory, a very simple conception, and by the aid of easy logic solve any problem in the gas laws, as illustrated above. The only numerical value that needs to be remembered is that  $0^{\circ}\text{C.}$  is  $273^{\circ}\text{A.}$

15. The following somewhat oversimplified derivation of the relation between pressure,  $p$ , number of molecules,  $n$ , mass per molecule (molecular weight),  $m$ , volume,  $v$ , and average molecular velocity,  $u$ , may prove helpful to some. Imagine a cubic box,  $l$  cm. on a side; a single molecule moving back and forth between opposite walls with velocity  $x$  would hit  $x/l$  times per second, with a force of  $2mx$  (twice the change of momentum) at each impact. The pressure exerted on these two walls is thus  $2mx^2/l$ . The velocity in the  $x$ -direction is, however, only one component of the total velocity,  $u$ , the relation being  $u^2 = x^2 + y^2 + z^2$ , where  $y$  and  $z$  are the component velocities in the two other directions. The total pressure exerted by 1 molecule on all six walls, is  $2mu^2/l$ . Since the area is  $6l^2$ , the pressure per sq. cm.,  $p$ , is  $\frac{1}{3}mu^2/l^3$ . But  $l^3 = v$ , the volume of the box, so that  $p = \frac{1}{3}mu^2/v$  for 1 molecule and  $p = \frac{1}{3}nmu^2/v$  for  $n$  molecules. Now,  $\frac{1}{2}mu^2$  is the average kinetic energy per molecule, which is, by the theory, assumed proportional to the temperature, provided that temperature is reckoned, not from  $0^{\circ}\text{C.}$ , but from the point where molecular velocity ceases, the real "absolute zero." Writing  $\frac{1}{2}mu^2 = kT$ , where  $T$  is the temperature on the new scale and  $k$  the universal "Boltzmann constant" of proportionality, we have,  $p = \frac{nkT}{v}$  (2).

It is interesting to see what magnitudes are represented by the velocities of gas molecules. We shall see later that 2 g. of hydrogen or 32 g. of oxygen equal  $nm$  and occupy a volume of 22,400 cc. at  $273^{\circ}\text{A.}$  and one atmosphere which is  $1.013 \times 10^6$  dynes per square centimeter. Substituting



in equation 1, we get 1840 meters per second for hydrogen and 460 meters per second for oxygen.

16. In drawing the various conclusions given above concerning the relations between pressure, volume, amount and temperature, we must remember that we have assumed that when the gases are sufficiently expanded the volume occupied by the molecules themselves is negligible compared with the volume of the vessel, also that they are so far apart and moving with such high velocity that their mutual attractions can be neglected. The higher the temperature and the lower the concentration, the more nearly do these assumptions correspond to the truth. On the other hand, as the temperature is lowered and as the concentration is increased, increasing deviations are to be expected from the behavior previously deduced, becoming more and more marked until the attractive forces become sufficient to cause the molecules to condense to the liquid state. The conditions under which this condensation takes place obviously depend upon the kind of molecules involved. With the gas helium, at a pressure of one atmosphere, the temperature must be lowered to  $4.5^{\circ}$  A. before liquefaction takes place.

17. **Partial Pressure of Different Gases in Mixtures.** The kinetic theory also enables us to predict correctly certain properties of gaseous mixtures. In the first place, we would expect the gas laws to hold for mixtures of gases as well as for pure gases, as is indeed the case. In the second place, we would expect the molecules of one species to maintain the same average kinetic energy at the same temperature regardless of the presence of any other species of molecules, and therefore **the part of the pressure which is due to the impacts on the vessel walls of one species, called the partial pressure of that gas, would be the same no matter what other gases are present.** This may be expressed by saying that the total pressure in a mixture of gases equals the sum of the partial pressures. This law is usually known as Dalton's Law. By way of illustration, let us suppose a closed vessel containing water and carbon dioxide gas maintained at a constant temperature. Some of the carbon dioxide will dissolve in the water. Suppose now that some other gas, say nitrogen, is injected into the same vessel. How would this affect the amount of carbon dioxide dissolved in



the water? Without the aid of the kinetic theory one might suppose that more carbon dioxide would be forced into the water, but from the molecular-kinetic standpoint we see that the number and momentum of the carbon dioxide molecules striking the water surface, upon which alone the solubility of the gas depends, are practically unaltered by the presence of the nitrogen molecules.

Again, suppose we consider two vessels of equal size, one evacuated and the other containing oxygen, both kept at the same temperature. If water is introduced into the first one, a little of it will vaporize, since the molecules of the liquid are in rapid motion with a velocity depending on the temperature, and certain molecules at the surface which have unusually high velocities may be able to escape the attraction of the liquid and go into the vapor phase. As the number of molecules in the vapor phase increases, there is a constantly increasing chance that some of them, moving more slowly than usual, will be caught into the liquid again, instead of rebounding at the surface. The concentration of molecules in the vapor state thus tends to become adjusted, so that there is an equilibrium or balance between the two phases such that the number of molecules of liquid vaporizing in a given time just equals the number of molecules of water condensing in the same time. The pressure of vapor necessary for this equilibrium depends on the nature of the liquid and on the temperature, increasing as indicated by the curve in Fig. 5. It is obvious that this pressure will not depend on the extent of the liquid surface, as an increase in surface has the same effect on the number of molecules vaporizing as it has on the number condensing, so that the net effect is zero.

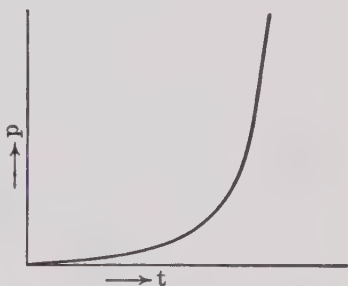


FIG. 5. Vapor pressure of a liquid.

Suppose, now, we admit water to the second vessel, containing oxygen. Evidently the tendency of molecules of liquid to escape will be the same as before, but the vaporized molecules will be unable to distribute themselves so rapidly throughout the vessel, since they must diffuse through oxygen molecules which collide with them and retard their progress. Hence the liquid will evaporate more slowly than in the previous case, where oxygen was absent, but eventually the molecules of water vapor will be distributed throughout the vessel just as if the oxygen were absent, and the partial pressure of the water vapor will be independent of the other gas (or gases) present.

**18. Relation between the Pressure of a Gas and Its Solubility in a Liquid.** When a gas is placed over the surface of a liquid, it dissolves to an extent dependent on the nature of the gas, the nature of the liquid, the temperature and the pressure of the gas. When no more gas will dissolve in the liquid, we have a state of equilibrium, in which the number of molecules of gas being caught into the liquid in a given time is the same as the number escaping.

Suppose, now, that more of the same gas is introduced into the space above the liquid. If the temperature is kept the same, the momentum of the molecules striking the surface of the liquid is unaltered, but the number so striking is increased, so that more of them enter the liquid than escape from it, and the added number of dissolved molecules finally increases the number escaping until it again equals the number entering. An increase, therefore, in the pressure of the gas above the liquid causes an increase in the amount of gas dissolved by it. We would naturally expect this amount dissolved to be proportional to the pressure, which is approximately true for gases which are not too soluble. This is known as **Henry's Law**.

**19. Avogadro's Rule.** One more consequence of the kinetic theory should be given at this time, as it will play a very important part in the reasoning in Chapter IV.

When two different gases are at the same temperature, the average kinetic energy of the two different kinds of molecules is the same. We conclude that this is true from the fact that when two different gases at the same temperature are mixed the total resulting pressure is the sum of the partial pressures each gas would have if the other were absent; hence the kinetic energy of neither is altered by the mixing, which can be the case only when they have the same kinetic energy before mixing. Let us then take, in two vessels of equal volume, such amounts of two different gases at the same temperature that their pressures will be the same. Now we have seen that the pressure of a gas depends upon the number of molecules, their kinetic energy and the volume they occupy, and upon no other factors. Since, therefore, we have chosen equal pressures, volumes and temperatures (and hence kinetic energies) the only other factor, the number of molecules in the two quantities of gas, must likewise be the same. In other words, **equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules.** This was first announced by an Italian physicist, Avogadro, in 1811, and is usually called **Avogadro's Rule** or Hypothesis. We will use it presently to measure the relative numbers of molecules involved in chemical reactions.

**20.** Those who followed the discussion in paragraph 15 can derive Avogadro's Rule quite simply from equation 2, since if we set  $p$ ,  $V$  and  $T$  equal for two gases then  $n_1 = n_2$ .

**21.** Other consequences of the kinetic theory may readily be drawn. For example, the molecules of a gas striking a compressing piston rebound with increased velocity just as is the case with a baseball struck by a batter; hence they are hotter and the process of compressing heats the gas, cf. Fig. 6*a*. The reverse is of course true, and a gas expanding by doing work on a retreating piston is cooled, cf. Fig. 6*b*. This occurs both in steam engines and gasoline motors. On the other hand, a gas leaking through a fine hole into a vacuum is not cooled, any more than a ball is retarded by passing through an open window, cf. Fig. 6*c*. However, if the gas is highly compressed, then, on expansion through an orifice

the mutual attractions of its molecules may be enough to cause retardation as they move apart, just as a ball is retarded when rising against the earth's gravitational attraction, cf. Fig. 6*d*. This effect is used in the liquefaction of air. The air is highly compressed, cleaned of moisture and carbon dioxide, cooled to remove the heat of compression, first by water,

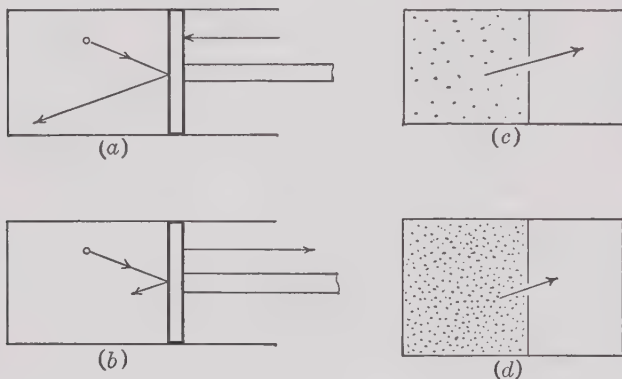


FIG. 6. Effect on molecular velocity of (a) compression, (b) expansion doing work, (c) expansion into a vacuum, (d) the same for a highly compressed gas.

then, in certain plants at least, by liquid ammonia, then by air that has already expanded and cooled itself. Part of this strongly cooled air then liquefies on expansion through an orifice.

### EXERCISES

It is recommended that the student remember that the purpose of the following exercises is not simply to get the correct answers, which might be achieved simply by substituting unintelligently in the formulas found in a high school text, but rather to stimulate the exercise of the imagination. Exercises 18 and 19 are particularly good tests of this ability.

1. What properties serve to distinguish solids, liquids and gases? State the distinctions in terms of the Kinetic Theory.

2. If a certain quantity of gas occupies 100 cc. at 3 atm., at what pressure will it occupy 60 cc. if the temperature remains unchanged?

*Ans.* 5 atm.

3. If 16 g. of oxygen is required to inflate a rubber balloon to a certain size at  $0^{\circ}\text{C.}$ , what weight of oxygen must be used to inflate it to the same size at  $20^{\circ}\text{C.}$ ?

*Ans.* 14.9 g.

4. Some gas occupies 100 cc. at  $127^{\circ}$  and 50 cm. pressure. To what temperature would it have to be cooled in order that a simultaneous decrease in volume to 60 cc. would produce no change in pressure?

*Ans.* —  $33^{\circ}$  C.

5. If an automobile tire is inflated to a pressure of 60 lb. per sq. in. at  $15^{\circ}$  C., what will the pressure become if the tire is heated to  $50^{\circ}$  by running?

*Ans.* 67.3 lb. per sq. in.

6. What proportion by weight of the air in an automobile tire must be allowed to escape in order to reduce its pressure from 70 lb. to 60 lb. per sq. in., the temperature remaining the same?

*Ans.*  $\frac{1}{4}$ .

7. A quantity of gas occupies a volume of 40 cc. at  $127^{\circ}$  C. At what temperature will its volume become 22 cc., the pressure remaining the same?

*Ans.* —  $53^{\circ}$  C.

8. At what temperature will a flask contain 3.30 g. of carbon dioxide gas at 1 atm. if it contains 2.00 g. at  $57^{\circ}$  C. and 1 atm.?

*Ans.* —  $73^{\circ}$  C.

9. To what temperature must an open flask be heated in order that one fifth of the gas which it contains at  $7^{\circ}$  C. shall escape?

*Ans.*  $77^{\circ}$  C.

10. If a balloon has a capacity of 480 cubic meters, how many tanks of hydrogen must be used to fill it if each tank has a volume of 0.300 cubic meters and contains hydrogen at a pressure of 40 atm.?

*Ans.* 41. (1 atm. left in tanks).

11. If 1 liter of a certain gas, measured at 76 cm. and  $0^{\circ}$  C., weighs 1.25 g., what would be the weight of 1 liter of the same gas at 60 cm. and  $47^{\circ}$  C.?

*Ans.* 0.84 g.

12. A tank contains 150 g. of hydrogen at 15 atm. and  $17^{\circ}$  C. What weight of hydrogen would escape if the tank were heated to  $100^{\circ}$  C. and the cock opened?

*Ans.* 142 g.

13. If the concentration of chlorine gas in a flask is 3.16 g. per liter at  $0^{\circ}$  C. and 1 atm., what will it be at  $47^{\circ}$  C., if the pressure is 0.8 atm.?

*Ans.* 2.16 g. per l.

14. A flask contained enough oxygen molecules to exert a pressure of 0.5 atm. upon the walls. If twice as many nitrogen molecules and three times as many helium molecules are introduced, what will be the pressure upon the walls?

*Ans.* 3 atm.

15. If water is introduced into an evacuated vessel at  $20^{\circ}$  C. the pressure inside the vessel becomes 17 mm. of mercury. If some air which has been standing over water at  $20^{\circ}$  C. is put into a flask to a pressure of 756 mm., a piece of quicklime introduced and the flask closed, what will the pressure become when the quicklime has absorbed all of the water vapor from the air?

*Ans.* 739 mm.

16. According to the Kinetic Theory how will the temperature of a gas be affected by expansion into a vacuum? Explain briefly.

17. Explain, in terms of the Kinetic Theory, why an automobile pump gets hot while pumping air into a tire.

18. State the effect, quantitatively where you can, of each of the following changes upon (a) the number of molecular impacts per second per square centimeter upon the containing walls and (b) the force of each impact.

(1) Gas in a cylinder with a movable piston, immersed in a large water bath, is expanded from 2 liters to 3 liters.

(2) The air pressure in an automobile tire is slowly pumped up from 20 lb. per sq. in. to 30 lb. per sq. in.

(3)  $\text{H}_2\text{S}$  gas is kept in a closed vessel at constant temperature until it has all decomposed into  $\text{H}_2$  and liquid sulfur.

19. Consider the following quantities for two gases, designated 1 and 2, respectively: pressure,  $p$ ; volume,  $v$ ; temperature,  $T$ ; molecular weight,  $m$ ; mean molecular speed,  $s$ ; number of molecules,  $n$ . If you are given the following relations between certain of these pairs of variables, you can draw conclusions regarding others. Indicate this conclusion in each of the following cases by writing in the sign,  $>$ , when the first is greater than the second (e.g.,  $p_1 > p_2$  means  $p_1$  is greater than  $p_2$ ), the sign,  $<$ , when it is less, and the sign,  $=$ , when it is equal to the second. If no conclusions can be drawn, write a question mark (?).

CONCLUSIONS FROM THE KINETIC THEORY. INDICATE BY WRITING IN THE APPROPRIATE SIGN,  $>$ ,  $<$ ,  $=$  OR ?

(a)  $m_1 > m_2$ , equal  $p$ ,  $v$ ,  $T$ ;

$s_1$  . . .  $s_2$

(b)  $m_1 > m_2$ , equal  $p$ ,  $v$ ,  $T$ ;

$n_1$  . . .  $n_2$

(c)  $p_1 > p_2$ ,  $m_1 > m_2$ , equal  $T$ ,  $n$ ;

$v_1$  . . .  $v_2$

(d)  $n_1 > n_2$ , equal  $p$ ,  $v$ ;

$T_1$  . . .  $T_2$

(e) Equal  $v$ ,  $n$ ,  $s$ ;

$p_1$  . . .  $p_2$ .



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# Chapter IV

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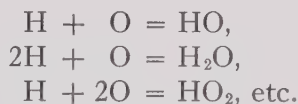
## *Molecular Weights*

**1. Choice of Formulas and Corresponding Atomic Weights.** In Chapter II we showed how the atomic theory, deduced from the law of conservation of mass and the law of simple multiple proportions by weight, could be expressed in a simple and comprehensive notation by the aid of which any one of the three factors, relative weights, formula and atomic weights, could be calculated from the other two. Now the relative weights may be found by experiment, but in order to get either of the other factors one of them must be known. Although we practiced with a number of formulas to become familiar with the meaning of the notation used, we did not show that the molecules of the substances referred to actually contained the numbers of atoms of the constituent elements signified by the formulas used, *e.g.*,  $\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{AsCl}_3$ .

To illustrate the problem we now face let us consider the formula of water. We know thus far only that the ratio of the weight of hydrogen to that of oxygen in water is approximately 1 to 8. This we learn by the analysis of water. If, now, the formula of water is  $\text{HO}$ , the relative weights of the atoms of hydrogen and oxygen are 1 to 8. But if the molecule of water is to be represented by  $\text{H}_2\text{O}$ , the relative weights of the single atoms would have to be 1 to 16. Again, if the formula is  $\text{HO}_2$ , then the relative atomic weights must be 1 to 4. Evidently we must bring to bear some criteria other than those thus far considered.

in order to select the correct formula and atomic weight ratio.

If we should try to represent the formation of water from its elements on the basis of the various assumptions as to its formula, we should have, as probable guesses, equations such as the following:



By suitable choice of atomic weights any of these, or others, as just explained, would conform to the experimental weight ratio. The essential point of difference lies in the number of molecules of the three substances.

Now we have, from the Kinetic Theory, a means of measuring the relative numbers of molecules for gaseous substances. It was shown in Chapter III that, by Avogadro's Rule, at equal temperatures and pressures, equal volumes of all gases contain the same number of molecules. Accordingly, if we determine the relative volumes of the gases taking part in a chemical reaction in which the temperature and the pressure are the same before and after the experiment, we may conclude that the relative numbers of molecules are in the same proportion as the volumes. If the above reaction is carried out at a temperature high enough to keep the water in the vapor state, it will be found that two volumes of hydrogen and one volume of oxygen give two volumes of steam. Accordingly, we conclude that two molecules of hydrogen and one molecule of oxygen would give two molecules of steam. Our equation must now be written so as to express these numbers of molecules. **Since the oxygen in one molecule is enough to give two molecules of steam, each containing oxygen, there must be more than one atom of oxygen in its molecule;** hence its formula must be not O but O<sub>2</sub>, or O<sub>4</sub>, etc. However, as we consider other reactions, we never find that one molecule of oxygen gives

more than two molecules of any other substances, so we assume the simplest formula,  $O_2$ . This limits the above equation to the following:



where  $n$  is some whole number.

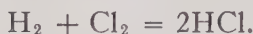
If this reasoning seems at all obscure it is because the reader has not trained himself to be as logical in dealing with unfamiliar as with familiar matters. Such training is an important element of education. One should be able to reason as correctly with  $x$  and  $y$  as with  $a$  and  $b$ , or with apples and boys. This requires training, for we naturally lean on our imaginations and become nervous when deprived of the prop. Let us illustrate the simple nature of the argument in the preceding paragraph by using familiar units.

If the  $\left\{ \begin{array}{l} \text{apples} \\ \text{atoms} \end{array} \right.$  in a certain number of  $\left\{ \begin{array}{l} \text{baskets} \\ \text{molecules of oxygen} \end{array} \right.$  have been distributed evenly among twice as many  $\left\{ \begin{array}{l} \text{boys,} \\ \text{molecules of steam,} \end{array} \right.$  each  $\left\{ \begin{array}{l} \text{basket} \\ \text{molecule of oxygen} \end{array} \right.$  must have contained at least two  $\left\{ \begin{array}{l} \text{apples.} \\ \text{atoms.} \end{array} \right.$

Anyone who has been admitted to college surely has brains enough to understand the conclusions regarding the apples per basket; anyone unwilling to persist till he can reason with equal assurance about atoms per molecule will not be well educated.

2. We still have to determine the number of atoms in the molecule of hydrogen. This is done, as in the case of oxygen, by finding the greatest number of other molecules, each containing hydrogen, that can be obtained from one molecule of hydrogen. This number has never been found greater than two, but often equal to two; hence we write  $H_2$ . The union of hydrogen and chlorine to form hydrogen chloride gas may be used for illustration. Experiment

shows that one volume of hydrogen and one volume of chlorine give two volumes of hydrogen chloride; hence one molecule of hydrogen and one molecule of chlorine give two molecules of hydrogen chloride, and the equation would be



Using this formula for hydrogen in our previous example, we write the equation for the formation of water

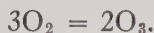


Finally, knowing the relative weights by experiment, and having deduced the formulas by the aid of Avogadro's Rule, we can assign values to the atomic weights. As explained before, one of these must be chosen arbitrarily, and we have seen how the number 16 has been assigned to the oxygen atom. Using this value, the weight of the oxygen molecule,  $\text{O}_2$ , becomes 32. By analysis of water we find that 32 parts of oxygen combine with 4.030 of hydrogen. The above equation shows that this represents four gram-atoms of hydrogen; hence one gram-atom of hydrogen is 1.008 g., and this number represents the atomic weight of hydrogen.

3. It is not long since the time when the simple way just explained for deciding upon the correct formula and atomic weight ratio was not understood. Many chemists, as late as 1858, used  $\text{HO}$  for the formula of water, while others used  $\text{H}_2\text{O}$ , and much confusion existed. Many criteria were used, other than those furnished by gas volumes, to determine the true formulas, but with only partial success. The table of atomic weights is thus the product of the thought and experimental work of a great many men.

4. We have seen that the molecules of hydrogen, oxygen and chlorine each contain two atoms. The same is true for nitrogen, fluorine, bromine and iodine. Another variety of

oxygen exists, called ozone, formed from oxygen by the silent electric discharge, with a diminution in volume in the ratio of 3 to 2, indicating that the equation must be written



The molecule of ozone, therefore, contains three oxygen atoms. The molecule of phosphorus vapor at low temperatures is  $\text{P}_4$ , at higher temperature  $\text{P}_2$ , that of sulfur may be  $\text{S}_8$ ,  $\text{S}_2$  or  $\text{S}$ , according to the temperature. When metals are vaporized their molecules seem always to consist of single atoms. The same is true of argon, and certain other gases recently discovered existing in small amounts in the atmosphere.

#### 5. Changes in Volume or Pressure in Gas Reactions.

The connection we have traced between the volumes of gases in chemical reactions and the relative number of molecules may be used conversely to deduce the change of volume or pressure to be expected when reactions take place between substances whose formulas are known. Consider, for example, the reaction represented by the equation



If this reaction is carried out at a temperature at which all of the substances represented are gaseous, then we see that three molecules have formed two. If the temperature and volume have been kept the same during the reaction, this will result in a decrease of the pressure to two thirds of its former value. If the temperature and pressure are the same as before, then the volume will be two thirds of its former value.

It is important, whenever an equation will be used to deduce relative volumes, to use the correct formulas of the substances in the gaseous form. For example, the same weight, 28 g., is indicated both by  $\text{N}_2$  and  $2\text{N}$ , but the

second formula is incorrect, and would lead us to expect twice the volume which would actually be involved.

**6. Volume of One Mole of Any Gas.** The double meaning attached to chemical symbols and formulas was explained in Chapter II, one referring to single atoms and molecules, and furnishing a basis for reasoning, and the other referring to the gram-atom and gram-molecule, or mole, and furnishing a basis for experimental work. Having determined that equal numbers of gaseous molecules are contained in equal volumes, at equal temperatures and pressures, and that the mole of all substances consists of the same number of molecules, it becomes important to ask what is the actual volume occupied by the mole of gas. This rests upon the measurement of gas densities, as illustrated by the following table:

GAS	WT. OF 1 LITER 0° C., 1 ATM.	VOL. OF 1 G. 0° C., 1 ATM.	G. PER MOLE	VOL. OF 1 MOLE 0° C., 1 ATM.
H. . .	0.08988 g.	11.126 l.	2.016	22.43 l.
O <sub>2</sub> . .	1.4291 g.	0.6998 l.	32.00	22.39 l.
N <sub>2</sub> . .	1.2507 g.	0.7995 l.	28.02	22.40 l.
NH <sub>3</sub> . .	0.7621 g.	1.3122 l.	17.03	22.35 l.

These values for the volume of the mole of gas under standard conditions, as well as others that might be added, are all very close to 22.4 liters, which may therefore be selected as the molal volume of a gas under standard conditions. (This is the volume of a cube 28.2 cm. or 11 $\frac{1}{8}$  inches on the side.) We may take this volume as the basis of our working definition of molecular weight, saying that **the molecular weight of a substance is the number of grams of it which occupy 22.4 liters when it is in the gaseous form and under standard conditions.** Very frequently, of course, substances cannot exist in the vapor state under these conditions, so that the relation between the weight and the volume of vapor must be found experimentally at some higher temperature, and perhaps lower pressure, after which it is possible to calculate the weight that 22.4 liters



of the vapor would have at  $0^{\circ}$  C. and 1 atmosphere, if no condensation took place.

7. We may illustrate by examples the various types of problems it is possible to solve with the aid of this relationship.

**Calculation of the Weight of a Given Volume or the Volume of a Given Weight of a Gas.** *Example:* What is the volume of 10 g. of  $O_2$  at  $127^{\circ}$  C. and 0.5 atmosphere? The answer to this is obtained by the following obvious steps:

32 g. of  $O_2$  occupy 22.4 l. at  $273^{\circ}$  A. and 1 atm.

32 g. of  $O_2$  occupy 44.8 l. at  $273^{\circ}$  A. and 0.5 atm.

32 g. of  $O_2$  occupy  $\frac{400}{273} \times 44.8$  l. at  $400^{\circ}$  A. ( $127^{\circ}$  C.) and 0.5 atm.

1 g. of  $O_2$  occupies  $\frac{1}{32} \times \frac{400}{273} \times 44.8$  l. at  $400^{\circ}$  A. and 0.5 atm.

10 g. of  $O_2$  occupy  $\frac{10}{32} \times \frac{400}{273} \times 44.8$  l. or 20.5 l. at  $400^{\circ}$  A. and 0.5 atm.

*Example:* What is the weight of 50 l. of  $CO_2$  measured at  $25^{\circ}$  C. and 3 atm.?

At  $273^{\circ}$  and 1 atm. 22.4 l. of  $CO_2$  weigh 44 g.

At  $273^{\circ}$  A. and 3 atm.  $\frac{1}{3} \times 22.4$  l. of  $CO_2$  weigh 44 g.

At  $298^{\circ}$  A. ( $25^{\circ}$  C.) and 3 atm.  $\frac{298}{273} \times \frac{1}{3} \times 22.4$  l., or 8.16 l., of  $CO_2$  weigh 44 g.

At  $298^{\circ}$  A. and 3 atm. 1 l. of  $CO_2$  weighs  $\frac{44}{8.16}$  g.

At  $298^{\circ}$  A. and 3 atm. 50 l. of  $CO_2$  weigh  $50 \times \frac{44}{8.16}$  g., or 270 g.

8. **Determination of the Relative Weights of a Gas and Air.** It is often important to know whether a gas is heavier or lighter than air. The proportion of nitrogen to oxygen in air is very nearly 4 to 1 by volume, so that in 22.4 liters of air four fifths of the molecules would be nitrogen and one fifth would be oxygen. Taking four fifths of 22.4 liters of nitrogen under standard conditions, weighing four fifths of

28.0 g., and mixing it with one fifth of 22.4 liters of oxygen, weighing one fifth of 32.0 g., we would get 22.4 liters of air weighing 28.8 g., under standard conditions. Suppose we wish to know the relative density of the following gases with respect to air:  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{Cl}_2$ . We can find their molecular weights with the aid of the atomic weight table, and conclude that 22.4 liters under standard conditions would have the following weights:  $\text{CO}_2$ , 44 g.;  $\text{NH}_3$ , 17 g.;  $\text{HCl}$ , 36.5 g.;  $\text{Cl}_2$ , 70 g.; air, 28.8 g. This shows at once the relative weight of each with respect to the air.

**9. Determination of Molecular Weight.** *Example:* What is the molecular weight of phosphorus vapor and what is its formula, given the atomic weight,  $\text{P} = 31.0$ , and the experimental determination that a flask having a volume of 583 cc. was filled with the vapor at  $310^\circ \text{C}$ . and a pressure of 756 mm., and that it was found on cooling to contain 1.49 g. of phosphorus? The molecular weight is found from the number of grams occupying 22.4 liters at  $273^\circ \text{A}$ . and 760 mm., which must therefore be calculated.

Since 1.49 g. of phosphorus vapor occupied 583 cc. at 756 mm. and  $583^\circ \text{A}$ .,

1.49 g. of phosphorus vapor would occupy  $\frac{756}{760} \times 583$  cc. at 760 mm. and  $583^\circ \text{A}$ .,

1.49 g. of phosphorus vapor would occupy  $\frac{273}{583} \times \frac{756}{760} \times 583$  cc. at 760 mm. and  $273^\circ \text{A}$ .,

1.49 g. of phosphorus vapor would occupy 0.2715 l. at 760 mm. and  $273^\circ \text{A}$ .,

$\frac{22.4}{0.2715} \times 1.49$  g., or 123 g., of phosphorus vapor would occupy 22.4 l. at 760 mm. and  $273^\circ \text{A}$ .

Since 123 g. would occupy 22.4 l. under standard conditions, if it did not condense, 123 is approximately the molecular weight. Since the atomic weight is 31, there are evidently 4 atoms in the molecule, so that the formula is  $\text{P}_4$ .

10. As another example we may determine the formula of a compound, found by analysis to contain 40 per cent of carbon, 6.67 per cent of hydrogen, and 53.33 per cent of oxygen, and of which 0.50 g. gave 328 cc. of vapor at 200° C. and 750 mm. We will first find the relative number of atoms of each element in the molecule of the compound. From the per cents given we may say that

40 g. C combines with 6.67 g. H and 53.33 g. of O

∴ 12 g. " " "  $\frac{12}{40} \times 6.67$  g. = 2 g. H and  $\frac{12}{40} \times 53.33 = 16$  g. O  
 or 1 g.-atom C " " 2 g.-atoms H and 1 g.-atom O  
 or 1 atom C " " 2 atoms H and 1 atom O.

The formula might therefore be CH<sub>2</sub>O. However, the same proportions by weight would be found if the formula were C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> or C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>, or any other multiple of CH<sub>2</sub>O. In order to distinguish between them we must therefore determine the number of grams per mole, which is numerically equal to the molecular weight.

Since 0.5 g. occupies 328 cc. at 750 mm. and 473° A. (200° C.), 0.5 g. would occupy  $\frac{750}{760} \times 328$  cc. at 760 mm. and 473° A., and 0.5 g. would occupy  $\frac{273}{473} \times \frac{750}{760} \times 328$  cc., or 187 cc. at 760 mm. and 273° A.

Now the weight of gas contained in 22.4 liters, or 22,400 cc., is 1 mole, and since 187 cc. weigh 0.5 g., 1 cc. would weigh 0.00267 g. and 22,400 cc. would weigh 22,400  $\times$  0.00267 g., or 60 g. Of the various multiples of CH<sub>2</sub>O the one having a molal weight of 60 g. is C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>; hence this is the correct formula.

11. Direct Relation between Volumes of Gases and Weights of Other Substances in Reactions. *Example:* When limestone is heated to a sufficiently high temperature, it decomposes, as represented by the following equation:





	$\text{CO}_2 \text{ (gas)} + \text{C (solid)} = 2\text{CO (gas)}$		
(2) Weight in grams	44	12	56
Number of moles	1	1	2
Volume at 0° C., 1 atm.	22.4 l.	$\frac{12}{d}$ cc.	44.8 l.
Number of mole- cules	$6 \times 10^{23}$	$6 \times 10^{23}$	$12 \times 10^{23}$

The last row of figures is added for the sake of interest, not because it will be used in problems. The other data represent all that is necessary in order to solve any problem involving weights, or volumes of gases, provided that one knows how to apply the gas laws to get the relation between the volumes of gases at standard conditions and at other conditions. It must be noted that this generalization connecting weights and volumes is possible only where gases are involved. With liquids and solids the densities of the particular substances must be determined by experiment.

**13. Molecular Weights of Dissolved Substances.** It is frequently impossible to determine the molecular weight of a substance from the volume of its vapor, owing to decomposition on heating. Sugar, for example, decomposes instead of vaporizing when heated, turning first to caramel and then charring. Some property other than the density in the vapor state is therefore necessary in order to determine its molecular weight, and to decide which multiple of its empirical formula,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , is the correct one. Hydrogen peroxide, likewise, is very unstable, except when in a dilute solution, decomposing often with explosive violence when in the pure state. Analysis shows that it contains twice as much oxygen in proportion to the hydrogen as does water; hence, having decided that water is represented by the formula  $\text{H}_2\text{O}$ , we may conclude that hydrogen peroxide must be represented by one of the formulas  $\text{HO}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}_3$ , etc. These are alike in the proportion of hydrogen to oxygen, 1 to 16, but differ in the total weight of the molecule, *i.e.*, the molecular weight. To distinguish between these possible formulas, therefore, we must find out whether the mole weighs 17 g. or 34 g. or 51 g., etc. For such substances the molecular weight must be determined under conditions such that the substance does not decompose, which is the case often in dilute solutions.

**14.** Among the properties of a solution which depend upon the molecular weight of the dissolved substance (called the solute) are the vapor pressure,



the boiling point and the freezing point. To understand the nature of the effect of a solute we may apply again the kinetic theory. If we have a pure liquid in contact with its vapor in a closed vessel, we imagine that there is a constant interchange of molecules between the two phases, molecules going from the liquid into the vapor phase at the same rate that others go from the vapor phase back into the liquid. If now, keeping the temperature constant, we add to the liquid in the closed vessel some molecules of another kind which are not volatile, and so cannot escape into the vapor phase, the number of molecules capable of escaping from the solution is now less than before, resulting in a smaller pressure of vapor above the liquid. If the new molecules introduced are attracted in about the same way as the molecules of solvent originally present, then we might expect that if the volatile molecules of solvent constitute, say, only 0.9 of the total number of molecules, their vapor pressure would be only 0.9 of what it is when the solvent is pure. This conclusion is borne out by experiment. This may be used to determine molecular weights, for if we find that a certain number of grams of solute in a certain number of moles of solvent lower the vapor pressure of the latter to, say, 0.9 of its value when the solvent is pure, then 0.9 of the total number of molecules are of the solvent and 0.1 are of the solute, from which we can calculate the number of grams per mole of solute.

**15. Example:** Pure carbon disulfide,  $\text{CS}_2$ , has a vapor pressure of 297 mm. at  $20^\circ \text{C}$ . It was found by experiment that 12.7 g. of iodine dissolved in 38 g. of  $\text{CS}_2$  lowered the vapor pressure of the latter to 270 mm. Given the atomic weight, 127, we wish to know the formula of dissolved iodine. Since 270 mm. is 0.909 of 297 mm., the number of moles of  $\text{CS}_2$  is now 0.909 of the total number, and the number of moles of iodine is therefore 0.091 of the total number, or 0.1 of the number of moles of  $\text{CS}_2$ . One mole of  $\text{CS}_2$  weighs 76 g., and therefore 38 g. is 0.5 mole. Since there are 0.1 as many moles of iodine as of  $\text{CS}_2$ , or 0.05 mole, then 12.7 g. of iodine is 0.05 mole, and 254 g. is 1 mole. Since the gram-atom of iodine is 127 g., there are 2 gram-atoms per mole and hence 2 atoms per molecule, so that the formula is  $\text{I}_2$ .

**16.** Instead of measuring the number of dissolved moles by the lowering of the vapor pressure of the solvent, the temperature being kept the same, we may, on the other hand, keep the pressure the same, say 1 atmosphere, and determine how much the temperature must be increased in order to make the vapor pressure of the solvent great enough to continue boiling, *i.e.*, we may measure the rise in the boiling point produced by the added solute. Although the relation between this rise and the number of moles of solute is not so obvious as that between the lowering of vapor pressure and the number of moles of solute, it is probably evident that it is chiefly



the number of added moles and not their kind that determines the rise in the boiling point, so that having determined this effect for one solute of known molecular weight, we can use it to determine the molecular weight of other solutes.

17. Just as it is harder to vaporize the solvent from a solution than it is from the pure solvent, so it is harder to remove it by any other means, such as freezing, and just as the boiling point of a solution of a non-volatile substance is higher than that of the solvent, so the freezing point of the solution will be lower, and will depend, likewise, only on the number of moles of solute in a given amount of solution. In addition, therefore, to defining a mole experimentally as the number of grams which, in the vapor state and under standard conditions, would occupy 22.4 liters, we may also define a mole as the number of grams which, dissolved in a specified amount of some solvent, will cause a certain rise in the boiling point or lowering in the freezing point. For water as solvent, the rise in boiling point is  $0.52^\circ$ , and the lowering in freezing point is  $1.86^\circ$ , when 1 mole of any solute is contained in 1000 g. of water. For other concentrations the effect is nearly proportional. These numbers have been calculated from the heats of vaporization and fusion, but the explanation of the method lies beyond the scope of this book. Confirmation is found in the large number of substances, such as alcohol,  $\text{C}_2\text{H}_5\text{OH}$ , bromine,  $\text{Br}_2$ , ether,  $(\text{C}_2\text{H}_5)_2\text{O}$ , and acetone,  $(\text{CH}_3)_2\text{CO}$ , which can exist both in the vapor state and in solution in appropriate solvents, which show approximately the same molecular weight in both cases.

18. *Example:* It was found that a solution of 7.29 g. of sugar in 100 g. of water had a freezing point  $0.395^\circ$  lower than that of water. What is the molecular weight of the sugar? For each 1000 g. of water in a solution of the same concentration there would be 72.9 g. of sugar. Now, 1 mole of sugar in this amount of water would produce a lowering of  $1.86^\circ$ , and since 72.9 g. produces a lowering of only  $0.395^\circ$ , which is  $\frac{0.395}{1.86}$  or 0.213 of the lowering produced by 1 mole, there must be only 0.213 of a mole present. If, then, 72.9 g. is 0.213 mole, 1 mole is  $\frac{72.9}{0.213}$  g. or 342 g. Comparing this with the empirical formula of sugar,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , as determined by analysis, we see that the simplest formula is the correct one.

### EXERCISES

1. Define (a) compounds, (b) solutions, (c) elements in terms of the atomic and molecular theories.
2. What is the distinction between a mole and a molecule? Give an example of the former.
3. What conclusion can you draw from the fact that 1 liter of phos-

phine gas,  $\text{PH}_3$ , can be decomposed to give 250 cc. of phosphorus vapor, measured at the same temperature and pressure?

4. What volume of oxygen is necessary to burn 3 liters of  $\text{H}_2\text{S}$  gas according to the reaction:  $2\text{H}_2\text{S} + 3\text{O}_2 = 2\text{H}_2\text{O} + 2\text{SO}_2$ ? *Ans.* 4.5 l.

5. State a simple piece of evidence to show that the molecule of oxygen contains two atoms.

6. If ordinary oxygen is  $\text{O}_2$ , how could you prove that ozone is  $\text{O}_3$ ?

7. How many moles of oxygen,  $\text{O}_2$ , are 40 g. of oxygen? *Ans.* 1.25.

8. (a) How many moles of  $\text{NO}_2$  gas are there in 23 g. of it? (b) What volume would 23 g. occupy under standard conditions?

*Ans.* (a) 0.5 mole; (b) 11.2 l.

9. A closed vessel contains ammonia gas at 1 atm. and  $27^\circ\text{C}$ . A spark is passed through the gas till it is all decomposed into hydrogen and nitrogen. What will the pressure be if the temperature is (a)  $27^\circ\text{C}$ ., (b)  $127^\circ\text{C}$ .? The equation for the reaction is:  $2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$ .

*Ans.* (a) 2 atm.; (b)  $2\frac{2}{3}$  atm.

10. Give the specific gravity of each of the following gases referred to air under the same conditions:  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{S}$ ,  $\text{Cl}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  vapor,  $\text{HCl}$ ,  $\text{NO}$ ,  $\text{SO}_2$ .

*Ans.* 0.97; 1.11; 0.97; etc.

11. What is the volume of 34 g. of  $\text{NH}_3$  at  $546^\circ\text{C}$ . and 4 atm.?

*Ans.* 33.6 l.

12. What would be the relative efficiencies of the following gases as filling for balloons:  $\text{H}_2$ ,  $\text{He}$ ,  $\text{CH}_4$ ?

*Ans.* 26.8: 24.8: 12.8.

13. How efficient is hot air, at a temperature of say  $200^\circ\text{C}$ ., in lifting a balloon? (Make reasonable assumptions for any further necessary data.)

14. (a) A certain compound of carbon and hydrogen contains 20% of hydrogen; the atomic weights are  $\text{H} = 1$  and  $\text{C} = 12$ ; what is its simplest formula? (b) What is its formula if 1.5 g. of the gas occupy 1.12 l. under standard conditions?

*Ans.* (b)  $\text{C}_2\text{H}_6$ .

15. How many liters of  $\text{CO}_2$ , measured (a) under standard conditions, (b) at  $22^\circ\text{C}$ . and 5 atm. pressure, could be obtained by heating 1000 g. of  $\text{CaCO}_3$ ?

*Ans.* (b) 48.4 l.

16. At a certain pressure and temperature 2 g. of  $\text{CO}_2$  occupied a volume of 1250 cc. What is the molecular weight of another gas 2 g. of which occupied a volume of 720 cc. under the same temperature and pressure?

*Ans.* 76.4.

17. What volume of  $\text{CO}$ , measured at  $0^\circ\text{C}$ . and 0.8 atm., could be obtained from 25 g. of carbon by the reaction:  $2\text{C} + \text{O}_2 = 2\text{CO}$ ?

*Ans.* 58.4 l.

18. A certain gas is known to have a formula of the type  $\text{CH}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_3\text{H}_3$ , etc. Given that 295 cc. of it weigh 0.317 g. at  $22^\circ\text{C}$ . and 1 atm., which formula is correct?

*Ans.*  $\text{C}_2\text{H}_2$ .

19. Write the equation for the combustion of CO to CO<sub>2</sub>, and interpret it in terms of (a) moles, (b) liters at standard conditions, (c) grams.

20. 4.0 g. of scandium react with an excess of HCl to give 3.054 liters of hydrogen at 0° C. and 760 mm. At. wt. of Sc = 44. (a) What weight of scandium is equivalent to 1 g. of hydrogen? (b) What is the formula of scandium chloride? (c) What would be the volume of hydrogen at 25° C. and 784 mm. if collected over water? Vapor pressure of water at 25° C. is 24 mm.

21. What is the formula of a gas containing 46.1% of carbon and 53.9% of nitrogen, 2.60 g. of which has a volume of 560 cc. at 0° C. and 2 atm.? *Ans.* C<sub>2</sub>N<sub>2</sub>.

22. If  $m$  grams of a gas occupy 22.4 liters at 1 atm. and 273° A., what volume,  $v$ , will  $w$  grams of it occupy at  $p$  atm. and  $T$ °?

$$\text{Ans. } v = 0.082Tw/mp.$$

23. Hydrogen peroxide contains 1 part by weight of hydrogen to 16 parts of oxygen, and a solution of 0.369 g. of it in 25 g. of water had a freezing point of - 0.805°. What is its formula? *Ans.* H<sub>2</sub>O<sub>2</sub>.

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# Chapter V

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## *The Relation of Chemical and Physical Properties to Atomic Structure*

1. The nature of chemical union prior to the last few decades was clothed in mystery. Such pictures of it as were drawn were the product of pure speculation. The older generation of living chemists had to accumulate their knowledge of chemical behavior piecemeal, with little to guide them in the way of general principles. The students of today, however, can be saved much of this long process by availing themselves of the deductive approach made possible by the flood of light recently thrown upon the structure of matter. This chapter is intended to serve as a framework.

2. **Atomic Structure.** Atoms are no longer regarded as hard, indivisible spheres, but are known, on the basis of numerous, independent evidences, to consist of smaller and simpler particles. The mass of an atom is practically all concentrated in a very small, positively charged **nucleus**. The nucleus of the hydrogen atom is a single **proton**, having unit positive charge— $1.59 \times 10^{-19}$  coulombs—and a mass of  $1.663 \times 10^{-24}$  grams or 1.0081 in terms of an atomic weight of 16.00 for the oxygen atom. The nuclei of other atoms consist, according to present evidence, of protons and **neutrons**, the latter having almost the same mass—1.0090—but electrically neutral, as their name implies. The nuclei have positive charges, therefore, which are integral multiples of the charge of the proton.

3. To balance the positive charge of the nucleus the atoms of free elements have the proper number of **electrons**. These are particles having a charge of the same magnitude as the protons, but of negative sign, so that an atom containing equal numbers of protons and electrons is electrically neutral. The mass of an electron is only  $\frac{1}{1836}$  the mass of a proton and an atom can gain or lose electrons with no appreciable change in mass.

4. The composition and mass of the nucleus are relatively unimportant in determining the chemical behavior of an atom; it is the charge alone which is important. Although nuclei are now regarded as made up of protons and neutrons instead, as formerly, of protons and electrons, the present uncertainty does not affect the following discussion.

5. The actual radii and relative sizes of these particles are as follows:

	RADIUS, CM.	RELATIVE SIZES
Oxygen atom . . . . .	$6 \times 10^{-9}$	1
Oxygen nucleus . . . . .	$5 \times 10^{-13}$	0.000,1
Electron . . . . .	$1 \times 10^{-11}$	0.002
Proton . . . . .	$2 \times 10^{-13}$	0.000,03

It is evident that an atom, like the solar system, is mostly empty space, in which light electrons are flying about a heavy nucleus.

6. The magnitude of the nuclear charge determines the number of electrons and this, in turn, determines the chemical behavior in the following way. The electrons tend to arrange themselves in groups, principally of 2 and 8, as shown in the following table for the first 20 elements.

7. We may note that the first group of electrons is complete with 2, the second and third each with 8. (We shall see later that the third group is capable eventually of increasing to 18, the fourth group first to 8, then to 18, then to 32.) These evidently represent stable groupings and we need not be surprised that the helium, with its pair, and neon and argon, with their outer octets, are very stable

atoms, and that other atoms tend to assume these stable structures by gaining or losing electrons, even at the expense of their electric neutrality.

8. Since it is only the outer electrons that are immediately concerned in chemical changes, we find it useful to distinguish them as **valence electrons**, since their number determines the combining value of an atom, due to the fact that the number of atoms of each element required to form a neutral compound is determined by the number of electrons each can gain or lose. The entire structure underlying the outer shell of valence electrons is usually called the **kernel** of the atom. The following scheme should help to make these terms clear.

Atom	Na	Cl	Ca	
Nucleus	+ 11	+ 17	+ 20	
Electrons				
1st group	2	2	2	} Kernel
2nd group	8	8	8	
3rd group	1	7	8	
4th group			2	} Valence electrons

9. We shall represent the kernel of an atom by its symbol in boldface type, remembering the + charge each kernel would have and the outer electrons that would have to be present in a neutral atom. The following comparison illustrates the relation between these kernel symbols and the ordinary symbols, using dots to denote valence electrons.

Ordinary symbol	H	H <sup>+</sup>	Cl	Cl <sup>-</sup>	Cl <sub>2</sub>	HCl	H <sub>2</sub> O
Kernel symbol	H·	H	· <b>Cl</b> ·	: <b>Cl</b> :	: <b>Cl</b> : <b>Cl</b> :	H: <b>Cl</b> :	H: <b>O</b> : H

10. It is also conceivable that the octet structure should be attained by the loss of all seven outer electrons, and this is indeed possible, although far less frequent. If no outside source of electrons is available, two atoms may share two



TABLE 1

ELEMENT	H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	A	K	Ca	Sc	Ti
Nuclear charge, + . . . . .	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
No. of electrons, - . . . . .	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Group 1. . . . .			1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8	8	8	8	4
Group 2. . . . .																						
Group 3. . . . .																						
Group 4. . . . .																						

electrons, giving each a partial ownership in a complete octet, forming molecules such as  $F_2$ ,  $Cl_2$  and  $Br_2$ .

An atom which is far from possessing an outer octet, such as Li, Be, Na, Mg, etc., shows little or no tendency to add electrons but rather reaches the octet structure, or, in the cases of Li, and Be, the stable pair by giving up electrons. For example, to remove one electron from a gaseous sodium atom, Na, with the structure  $+11 - 2, - 8, - 1$ , requires a potential of but 5.1 electron-volts, while to remove an electron from a fluorine atom, F, with the structure  $+9 - 2, - 7$ , requires 16.9 electron-volts. In harmony with this difference we find that elements having a small number of electrons in the outermost level hold their electrons so loosely in the solid state that they readily conduct the electric current, which, with metallic luster, is the most distinctive characteristic of metals. Elements whose outer octets are completed, whether alone or by sharing electrons, are non-conductors and non-metallic.

**11.** This structural distinction between metals and non-metals is obviously related to their respective chemical behaviors. If a metallic atom, say sodium, Na, which has the structure,  $+11 - 2, - 8, - 1$ , be brought into proximity with a chlorine atom, which is  $+17 - 2, - 8, - 7$ , it is evidently possible for both atoms to reach the octet structure by the passage of an electron from the Na to the Cl giving  $+11 - 2, - 8$  for sodium and  $+17 - 2, - 8, - 8$  for chlorine. The former will thus have one electron too few or one proton too many, and we represent it by  $Na^+$ , and the latter will have one additional electron, becoming  $Cl^-$ . These two charged atoms will now attract each other to form a molecule of sodium chloride, if in the gaseous state, or, if in the solid state, a lattice of alternating  $Na^+$  and  $Cl^-$ , shown in Fig. 4, page 303. In the crystal of sodium chloride, common salt, the sodium is therefore positive and the chlorine negative. The hardness of the crystal is chiefly the result of the electrostatic forces between these charged atoms.

**12. Non-polar, Polar and Ionic Compounds.** As stated above, two like atoms usually combine by sharing outer electrons, if possible, so as to complete pairs and octets, as illustrated by chlorine in Fig. 1. The molecule is symmetrical and electrically neutral, and is called **non-polar**. If the atoms differ somewhat in their affinity for electrons due to differing sizes or structures, the bonding or shared electrons will be closer to, or spend more of the time traveling about one atom than the other, making this atom on the whole

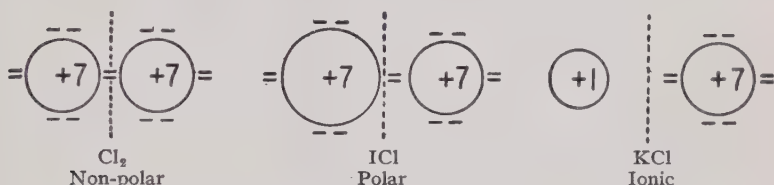


FIG. 1. Types of molecules.

more negative, as illustrated by iodine chloride, Fig. 1. Such a molecule is called **polar**. If the difference in electron affinity is sufficiently great, the outer electrons of the one may be completely lost to the other so that there is no true chemical bond but only the electrostatic attraction of the now positive and negative atoms for each other, as illustrated by potassium chloride. Such a molecule is called **ionic**, since the two parts are easily detached from each other on going into solution where they are free to wander off in different directions.

**13.** The degree of polarity, or displacement of + and - charges in a molecule is expressed by its **dipole moment**. The transition from non-polar through increasingly polar to ionic compounds is illustrated in Table 2.

The dipole moment often gives important evidence of molecular structure. For example, the large moment of the water molecule shows that it is not linear and symmetrical as represented by HOH, but approximately right angled, as represented by  $\text{HO} \begin{smallmatrix} \text{H} \end{smallmatrix}$ .

TABLE 2

## POLARITY

(The figures are for dipole moment  $\times 10^{18}$  electrostatic units)

ELECTRON DISPLACEMENT				
Zero	Increasing			Complete
H <sub>2</sub> , Cl <sub>2</sub>	HI,	HCl,	HF	NaCl
0 0	0.4	0.6	2	
PI <sub>3</sub>	PBr <sub>3</sub>	PCl <sub>3</sub>	SbCl <sub>3</sub>	BiF <sub>3</sub>
0	0.6	1.0	3.1	
H <sub>2</sub> Te	H <sub>2</sub> Se	H <sub>2</sub> S	H <sub>2</sub> O	MgO
0		1.0	1.9	

14. A study of dipole moments indicates that the negative character of some of the commoner non-metallic elements increases in the following order:

Sb, Te, H, As, P, Se, I, S, C, Br, Cl, N, O, F.

15. **Types of Crystal Lattices.** The various types of atoms and molecules arrange themselves in solid crystal lattices of rather distinct kinds with characteristic properties. Metallic atoms hold their electrons so loosely that even when massed together in the solid form the electrons can migrate more or less freely through the solid under the impulse of an electric field giving metallic conduction, the most distinctive property of metals. This is crudely illustrated in Fig. 2*a*. Moreover, since the positive "kernels" of the atoms—the atoms stripped of their outer electrons—are not bound to each other by specific bonds, they can be displaced relatively to each other without destroying the general attraction between kernels and electrons; hence the metals are ordinarily malleable.

Ionic substances, on the other hand, form crystals with alternately + and - atoms or, better, ions, which are too large to change places unless the structure is melted and greatly expanded; hence they are non-conductors in the solid form but conductors in the liquid state. To split the

crystal requires the overcoming of the electrostatic forces between the ions. They are not malleable or plastic since the sliding of one layer over another would bring together ions of like sign which would repel each other resulting in breaking the crystal before a new position of attraction is attained.

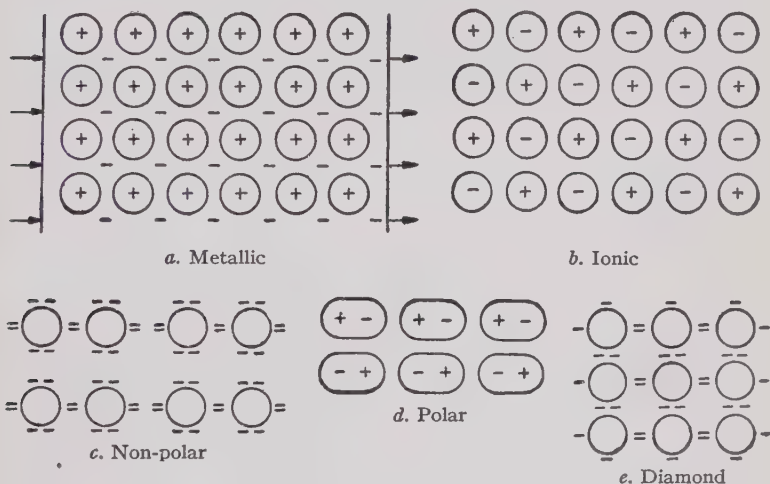


FIG. 2. Types of solid lattice.

Non-polar molecules and the single stable atoms of helium, neon, argon, etc., exert no electrostatic attractions upon each other but only a relatively weak force due to a general interaction of the rapidly moving electrons of one molecule with those of another, analogous, very roughly, to the interaction of vibrating tuning forks. Non-polar substances, therefore, are relatively soft, and are easily melted and vaporized. A number of the lighter molecules are gases at ordinary temperatures and pressures. Figure 2c represents a crude picture of a lattice of such molecules.

If the molecules are more or less polar we may expect them to strive for crystal arrangements in which oppositely charged parts of molecules are as near as possible together, giving enhanced attractions, melting points and crystal

strengths, other things being equal, as in Fig. 2*d*. In the liquid state, unlike the ionic substances, they cannot conduct the electric current by migrating independently to the poles, but they will tend to orient, except as opposed by thermal agitation, so that the charged ends of the molecules will lie in the direction of oppositely charged plates thrust into the liquid, as illustrated in Fig. 3.

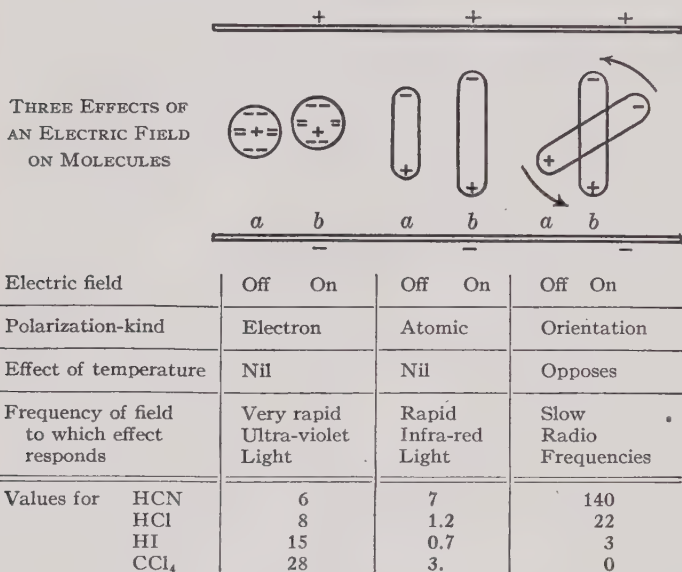


FIG. 3.

This figure illustrates three effects of applying electric fields to molecules. The first is the displacement of electrons with respect to nuclei; the second the stretching or bending of molecules, called atomic polarization; the third, the orientation of dipoles already existing within the molecule. The distinguishing characteristics of each effect are stated.

One other important lattice type exists, that represented by diamond. Carbon atoms have 4 outer electrons, as shown in Table 1. When 2 such atoms form a chemical bond



by sharing a pair of electrons the possibilities of sharing are not exhausted, as they are with chlorine atoms, but each can form electron-pairs with 3 other atoms. The result is represented in 2 dimensions by Fig. 2*e*. Actually each atom has 4 others around it arranged like the corners of a tetrahedron as illustrated in Chapter XVIII, Fig. 1. We see that there are no molecules of carbon in such a crystal, but that all the atoms are firmly bound together with electron-pair bonds, continuing throughout the crystal. To scratch or split such a crystal would require the rupture of a large number of these bonds, which are particularly strong with carbon due to its small atomic size. In fact, carbon is the hardest known substance, and neither dissolves nor vaporizes at any ordinary temperature.

**16. Relative Stabilities of Molecules.** In the cases of compounds in which the atoms may be regarded as definitely positive or negative by reason of the passage of electrons from the metallic to the non-metallic atoms, we may relate the stability of the compound in large part to the ease with which the electrons can be detached from the former and acquired by the latter. If the formation of one compound from its elements liberates more energy than the formation of another it is evident that to recover the free elements from the former would require more energy, whether electrical or chemical, than in the case of the latter; the former is therefore more stable. This energy of formation may be divided into a number of parts corresponding to carrying out the synthesis in a number of distinct steps. For example, if one mole (58.5 g.) of solid sodium chloride is to be synthesized from solid sodium and gaseous chlorine, instead of allowing the elements to react with each other directly to form the salt, a process which liberates 98 kg. cal. of heat per mole of NaCl, it is possible to melt one gram-atom of sodium, Na (solid), with absorption of its heat of fusion, next to vaporize it to give gaseous atoms, Na (gas), absorbing its heat of vaporization, then to strip it

of its outer electron, giving  $\text{Na}^+$  (gas), then let it unite with  $\text{Cl}^-$  (gas), prepared by splitting  $\text{Cl}_2$  (gas) into atoms,  $\text{Cl}$  (gas), and adding an electron per atom, to give gaseous  $\text{NaCl}$  molecules, which are then liquefied, and finally solidified.

This synthesis in steps is indicated in the following diagram along with the amount of heat, in kg. cal., involved in each step. A  $+$  sign means that heat has been absorbed, increasing the heat content of the material involved, and a  $-$  sign that heat has been evolved or lost.

TABLE 3

						$\frac{1}{2}\text{I}_2$ (solid)	
						$\downarrow + 7$	
						$\frac{1}{2}\text{I}_2$ (gas)	
						$\downarrow + 18$	
						$\text{I}$ (gas)	
						$\downarrow - 79$	
						$\text{I}^-$ (gas)	
						$\downarrow - 105$	
						$\text{KI}$ (gas)	
						$\downarrow - 43$	
						$\text{KI}$ (solid)	
						$- 79 \text{ kg. cal.}$	

the weather by looking at the new moon, to see whether its horns point up or down. We are impressed by claims that a single patent will cure many ailments, from dandruff down to athlete's foot. We vote for a candidate who promises to bring prosperity by means of some single, simple formula. The trouble is that matters are seldom so simple. The weather forecaster, spending all his time on the job, using a variety of criteria, still makes mistakes. Individuals and society spend part of the time recovering from the effects of absurdly simple panaceas.

Physical scientists have, for the most part, learned to be sceptical about explanations that are too simple. They have learned that there are about 92 elements, not four, "earth, air, fire, and water"; that the law of gravitation is not an adequate basis for a system of physics; that the behavior of electrons cannot be predicted from that of baseballs. Political and economic problems are still more complicated, and we should learn to distrust the social scientist who offers in a single palatable and intoxicating elixir to cure a sick social and economic system. We should learn that a spree and a cure may begin with similar feelings of elation but they end very differently.

**18.** It may be worth while to simplify a problem provided we remember what we have done and do not rely too heavily on the result. We decide in the morning whether or not to take along an umbrella on the basis of an admittedly unreliable prediction regarding the weather. After all, most of us can do better than tossing a coin to protect ourselves from getting wet. Indeed, the making of an accurate analysis of a problem may take so long, even when we know how, as not to be worth the effort. We find, fortunately, that we can correlate chemical stabilities with only a small proportion of error if we focus our attention on only a few of the factors presented in paragraph 16. In that case it is important only not to be surprised if we make a few mistakes.

TABLE 4  
HEAT IN KG. CALS. EVOLVED IN FORMATION PER GRAM-ATOM OF  
NEGATIVE ELEMENT

	OXIDES	CHLORIDES	IODIDES	CHLORIDES IN VERY DILUTE AQUEOUS SOLS.
Potassium . . . .	186	105	79	418
Sodium . . . . .	199	98	70	407
Calcium . . . . .	152	104	64	354
Aluminum . . . .	129	56	24	265
Zinc . . . . .	85	49	25	160
Iron (ferrous) . .	64	41	24	127
Tin (stannous) . .	70	40	18	88
Lead . . . . .	52	43	20	84
Hydrogen . . . .	66	41	— 6	83
Copper (cuprous) .	40	33	16	49
Silver . . . . .	7	30	15	31
Gold (aurous) . .	—	10	2	—

It is evident from the values in the table that, while the stability of a compound depends upon a number of factors, the electron changes are comparatively large; hence the tendency of an element to become positive or negative in a compound, *i.e.*, to lose or gain electrons, largely determines its stability. This will be discussed at more length later (Chapters XVI and XVII) in relation to atomic structures, and we will content ourselves here with simply giving a list, in Table 4, of some of the elements arranged roughly according to the stabilities of their compounds. The order is not quite uniform because the charged atoms do not arrange themselves in the same patterns in crystals of different compounds.

19. The order of the elements in Table 4 is worth remembering. This will not be difficult for one who will see its correlation, first with its historical significance. The noblest metal in the list, gold, has the greatest tendency to retain its electrons in the metallic state rather than to become positive in compounds, and, accordingly, has doubtless been known from earlier times than any other metal. Neither gold nor silver, however, were sufficiently abundant

to have any great cultural significance. Copper, on the other hand, is more abundant and is easily obtained from its ores and was the first metal to play a significant rôle in making tools and utensils. The alloy of copper with tin gave bronze, which is harder than either, and gave rise to the "bronze age." Iron is harder to obtain, hence the "iron age" came later. Only in recent times have metals such as sodium and aluminum been obtained. The order of the elements in Table 4 can be further correlated with their ordinary properties and uses. For example, gold is not subject to corrosion, silver tarnishes slightly, copper and lead more readily, but they can still be used where iron would rust badly. Aluminum seems to be stable but this is because the thin oxide coating first formed is very adherent and impervious; if the surface is wet with mercury the film no longer adheres and the metal oxidizes with great rapidity.

**20. Salts, Acids and Bases.** Substances which crystallize in ionic lattices are usually called **salts**, by analogy with NaCl, common salt. Most of them are more or less soluble in water, whose polar molecules (cf. paragraph 12) are able to attract the ions of the salt crystal sufficiently to overcome the forces holding them in the lattice. They are then able to wander about independently in the solution (cf. Chapter VIII).

The ions of salts are not confined to single charged atoms, but may consist of charged groups. Figure XVIII-5 represents the structure of such salts as  $\text{CaCO}_3$  and  $\text{NaClO}_3$ , where the ions are  $\text{Ca}^{++}$  and  $\text{CO}_3^{--}$  or  $\text{Na}^+$  and  $\text{ClO}_3^-$ , respectively. The following polyatomic ions are frequently encountered:

$\text{SO}_3^{--}$ sulfite	$\text{C}_2\text{H}_3\text{O}_2^-$ acetate
$\text{SO}_4^{--}$ sulfate	$\text{ClO}_3^-$ chlorate
$\text{CO}_3^{--}$ carbonate	$\text{ClO}^-$ hypochlorite
$\text{NO}_3^-$ nitrate	$\text{NH}_4^+$ ammonium
	$\text{Ag}(\text{NH}_3)_2^+$ silver ammonia complex.

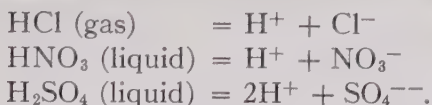


Such ions, like monatomic ions, owe their charges to an excess or deficiency of electrons.

21. There are a number of hydrogen compounds which, although not giving ionic lattices, react with water to give hydrogen ion, which may be written  $H^+$  (aq.),  $H_3O^+$  (i.e.,  $H_2O + H^+$ ), but is usually abbreviated to  $H^+$ , the water of hydration being understood. Such a solution is readily recognized as acid by such familiar tests as sour taste, reaction with base metals, such as zinc, to produce hydrogen,  $2H^+ + Zn = H_2 + Zn^{++}$ ; reaction with a carbonate to produce  $CO_2$  gas,  $2H^+ + CaCO_3$  (solid) =  $Ca^{++} + H_2O + CO_2$ ; and colors imparted to certain highly colored substances called indicators (cf. Chapter XIII). There are a number of more or less familiar acids which we may recall and characterize briefly. Hydrochloric acid,  $HCl$ , is a gas when in the pure state, but it is very soluble in water, forming the solution known industrially as "muriatic acid." Sulfuric acid,  $H_2SO_4$ , in the absence of water, is a dense, syrupy liquid, and has the trade name, "oil of vitriol." It is manufactured in larger quantities than any other substance for purely chemical purposes. Nitric acid,  $HNO_3$ , is a fuming, corrosive liquid extensively used to dissolve the nobler metals and in the manufacture of explosives. Acetic acid,  $HC_2H_3O_2$  (only one of the hydrogen atoms of which has acid properties), is the acid of vinegar. Phosphoric acid,  $H_3PO_4$ , is used in the phosphate drinks at soda fountains. Boric acid,  $H_3BO_3$ , or "boracic acid," is a solid giving a solution of very faintly acid properties. It finds use as a mild antiseptic. Oxalic acid,  $H_2C_2O_4$ , a solid in the pure state, finds frequent use as a chemical reagent. The various fruit juices contain characteristic acids, such as citric acid, found in lemons, tartaric acid in grapes, malic acid in apples, etc.

When acids dissolve in water, there is formed, along with  $H^+$ , an equivalent amount of negative ion, e.g.,





**22. Bases.** Certain solid lattices contain the hydroxide ion  $\text{OH}^-$  which is liberated, if the substance is soluble, on going into water solution. Such substances are called bases. The positive ion is nearly always that of a metal. Most of them are insoluble in water, or nearly so, the chief exceptions being sodium hydroxide,  $\text{NaOH}$ , sometimes called "caustic soda," potassium hydroxide,  $\text{KOH}$ , sometimes called "caustic potash," the solution of which is often called "lye," and barium hydroxide,  $\text{Ba(OH)}_2$ . Calcium hydroxide,  $\text{Ca(OH)}_2$ , "slaked lime," is sparingly soluble; its solution is known as "lime water." To these should be added ammonium hydroxide,  $\text{NH}_4\text{OH}$ , formed when ammonia gas,  $\text{NH}_3$ , is dissolved in water. The solid bases, especially the first two, are often called alkalis, and their solutions alkaline.

The most significant property common to bases is their ability to neutralize acids. If the base and acid are both soluble and largely split into ions, the reaction is simply,  $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$ . If the base is insoluble, for example,  $\text{Pb(OH)}_2$ , and the acid soluble, the reaction is expressed by  $\text{Pb(OH)}_2 + 2\text{H}^+ = 2\text{H}_2\text{O} + \text{Pb}^{++}$ . Of course, in order to have a solution of  $\text{H}^+$  some negative ion must be present, *e.g.*,  $\text{NO}_3^-$ , but where this does not take part in the reaction there is no more reason for representing it in the equation than there is to include the vessel, the operator or other necessary concomitants.

The soluble bases likewise can be recognized, like acids, by the colors they give to indicators. We shall see that it is possible by selecting proper indicators to construct a scale to measure all degrees of acidity and alkalinity (*cf.* Chapter XIII).

**23. Basic and Acidic Oxides; Anhydrides of Bases and Acids.** Certain oxides of metals can react with water to produce bases, *e.g.*,

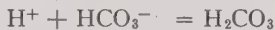
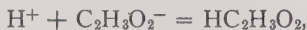


or, they may remain after a base is dehydrated by heating; or, again, they may neutralize an acid directly, without first reacting with water, *e.g.*,  $\text{CaO} + 2\text{H}^+ = \text{H}_2\text{O} + \text{Ca}^{++}$ . Their close relation to bases is justification for calling them **basic oxides** or **basic anhydrides**, or even, briefly, bases.

Certain other oxides, chiefly those of non-metals, react with water to yield  $\text{H}^+$ , *e.g.*,  $\text{H}_2\text{O} + \text{SO}_3 = \text{H}_2\text{SO}_4 = 2\text{H}^+ + \text{SO}_4^{--}$ , hence may be called **acidic oxides** or **acid anhydrides**.

**24.** There are in use at present three systems of acids and bases. The first and simplest is particularly appropriate for aqueous solutions since it is based upon the two ions which unite to form water,  $\text{H}^+$  and  $\text{OH}^-$ . An acid is any substance which gives  $\text{H}^+$  and a base any substance which gives  $\text{OH}^-$ .

**25.** A different system has proved useful particularly in dealing with solvents other than water. This defines an acid as above, although the  $\text{H}^+$  is now not hydrated, but a base is any substance which can "accept" or unite with  $\text{H}^+$ . The ion,  $\text{OH}^-$ , is thus only one of many bases, others being indicated by reactions such as the following:

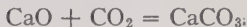


It makes no difference whether the substance uniting with the  $\text{H}^+$  and the product are charged +, - or 0.

**26.** A third system is based on the fact that there is no great distinction between the reaction of a base with an acid, in the simple water system, and the union of a basic oxide and an acid oxide, for example,



and



The chemist, ever since the days of Berzelius, and the mineralogist as well, find it convenient to think in terms of a scale of relatively basic and acidic oxides as follows:

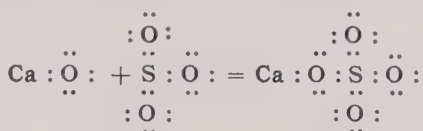
MOST BASIC

MOST ACIDIC

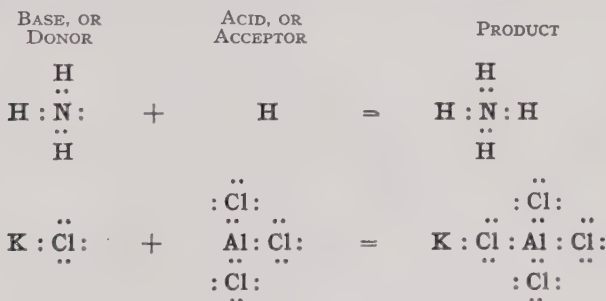


The farther apart two oxides are on this scale the stronger their tendency to combine.

The nature of the union is seen if we write the formula in terms of kernels and valence electrons, *e.g.*,



The  $\text{SO}_3$  unites with the  $\text{CaO}$  because it lacks the pair of electrons that completes the octet around the sulfur. The  $\text{CaO}$  is an "electron donor" and the  $\text{SO}_3$  is an "electron acceptor." A base may therefore be defined as a donor and an acid as an acceptor. The presence or absence of full octets usually gives the clue to basic or acidic possibility. The classification is not limited to oxides, as shown by the following:



27. Much futile argument can be indulged in by trying to decide which of these systems is "right" and which "wrong." The only question that should be asked is, which is most useful. The answer to this depends on what one is trying to do. Each represents a particular classification of phenomena, useful for certain purposes. Hammers and saws are not, in themselves, either right or wrong. The former are appropriate for driving nails, the latter for cut-

ting boards. So the chemist, if he is dealing only with water solutions, may find the  $H^+$  and  $OH^-$  system entirely adequate, while if he is dealing with organic reactions the "proton-donor-acceptor" system may be preferable. Again, the geochemist or investigator of high temperature reactions, from which hydrogen compounds are usually absent, will doubtless prefer the "electron-donor-acceptor" system. The wise man will preserve his ability to change from one to another as easily as a musician can shift from base to treble clef.

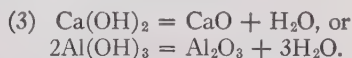
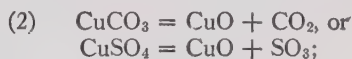
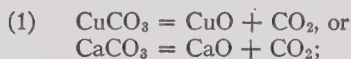
### EXERCISES

1. What is the characteristic difference between the structures of the atoms of metallic and non-metallic elements?

2. What is meant by each of the terms: electron, proton, kernel, nucleus, noble, metal, alkali, alkaline reaction, neutralization, anhydride?

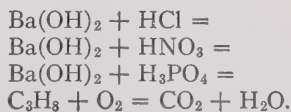
3. Determine, by subtracting  $H_2O$  in proper proportion, what are the anhydrides of the following substances:  $HNO_3$ ,  $H_2CO_3$ ,  $Fe(OH)_3$ ,  $Fe(OH)_2$ ,  $H_3PO_4$ ,  $HPO_3$ ,  $H_3PO_3$ ,  $CuOH$ ,  $H_2SO_3$ .

4. Which substance in each of the following pairs would decompose more easily, on heating, in the manner represented by the respective equations?



5. Which of the following metals would replace copper from a solution of  $CuCl_2$ : zinc, iron, platinum, aluminum, gold, mercury, sodium, silver?

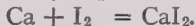
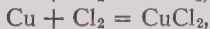
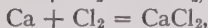
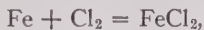
6. Complete the following equations:



7. Give, by formulas, two examples of each of the following: (a) alkali, (b) acid, (c) basic anhydride, (d) radical, (e) halide.

8. Knowing that zinc displaces copper from its chloride, would you expect the decomposition of  $ZnCl_2$  or of  $CuCl_2$  to require the greater electrical energy?

9. Which of the following reactions would you expect to take place with least evolution of heat, and which with the greatest?



10. Given that Li has 1 valence electron, Be has 2, C has 4, O has 6, and F has 7, state whether the following substances would be primarily ionic, electron pair bonded, or metallic. Also give the formula for each compound. (a) Li element, (b) O element, (c) F element, (d) compound of Be and F, (e) compound of Li and O, (f) compound of Li and F, (g) compound of O and F.

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## Chapter VI

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### *Concentration, Acidimetry and Alkalimetry*

1. The determination of the composition of any material is termed its **analysis**. **Qualitative analysis** is the determination of the kinds of matter composing the material; **quantitative analysis**, their amounts. The qualitative analysis of a mineral would give the information that it contains certain elements; its quantitative analysis would yield the amount of each. Quantitative analysis may be carried out by separating each constituent from the others in a form that can be weighed; this is called **gravimetric analysis**. For example, the amount of sulfuric acid in a solution may be determined by adding a solution of barium chloride, which produces a nearly insoluble **precipitate** (meaning a substance thrown down) of barium sulfate; this is filtered out on a suitable filter, dried and weighed. The amount of sulfuric acid present in the sample of solution analyzed can then be calculated from the relation that 98.08 g. of  $\text{H}_2\text{SO}_4$  yields 233.45 g. of  $\text{BaSO}_4$ .

2. There is another procedure, called **volumetric analysis**, where the amount of constituent is determined from the amount of a **reagent** (a reacting substance) necessary to complete some reaction with it, the amount of the reagent being found by having it in a solution of known concentration and measuring the volume of this solution necessary to complete the reaction, a process called **titration**. This method is usually preferred to the gravimetric method on account of its greater rapidity. Since it is important not



only for analysis but for many other purposes to have clear ideas respecting concentration, we will use volumetric analysis at this point to develop them.

The amount of an acid or alkali present in a solution is usually determined by volumetric analysis, since the exact amount of the one necessary to neutralize the other is easily determined by the aid of an indicator which shows the **end-point** of the titration. Suppose that we wish to determine the amount of sulfuric acid in, say, 50.0 cc. of a certain solution. We can titrate it in the presence of an indicator with a solution of NaOH of known concentration, say 10.0 g. per liter, using a **buret**, a tube provided at its lower end with a stopcock and graduated in cubic centimeters so that the volume of solution used can be read. Suppose that 20.0 cc. of the alkaline solution is necessary to neutralize the acid, as shown by the change of color of the indicator. Since 1000 cc. of the alkaline solution contain 10.0 g. of dissolved NaOH, 20.0 cc. of it contain  $0.02 \times 10.0$  g. or 0.200 g. To calculate how much sulfuric acid this can neutralize we write the equation,  $2\text{NaOH} + \text{H}_2\text{SO}_4 = 2\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$ , from which, by the aid of the atomic weights, we see that  $2(23.0 + 16.0 + 1.0)$  or 80.0 g. of NaOH can neutralize  $2.0 + 32.0 + 4 \times 16.0$  or 98.0 g. of  $\text{H}_2\text{SO}_4$ . Then 1.00 g. of NaOH can neutralize  $\frac{1}{80} \times 98.0$  g. or 1.225 g. of  $\text{H}_2\text{SO}_4$  and 0.200 g. of NaOH, the amount used in the titration, can neutralize 0.245 g. of  $\text{H}_2\text{SO}_4$ , which is the amount in the 50.0 cc. sample of the acid solution. It is not necessary for this purpose to write an equation in ionic form since acids or bases which are not completely ionized (cf. Chapter VIII, paragraph 14) are titrated to the same end-point as those which are.

3. The amounts of acid and alkali involved in the neutralization are much more simply expressed if the mole is used as the unit instead of the gram. Instead of saying that 80 g. of NaOH can neutralize 98 g. of  $\text{H}_2\text{SO}_4$ , we write simply that 2 moles of NaOH can neutralize 1 mole of  $\text{H}_2\text{SO}_4$ .

We should then express the concentration in terms of moles per liter, and 10.0 g. of NaOH per liter becomes 0.25 mole per liter since 40 g. of NaOH is 1 mole. **We designate concentration in terms of moles per liter by the letter *M* following the number and preceding the formula, thus 0.25 *M*-NaOH means a solution containing 0.25 moles of NaOH for every liter. It should be noted carefully that it expresses a concentration of NaOH, not an amount; thus:**

1 liter	of 0.25 <i>M</i> -NaOH	contains	0.25	mole of NaOH
2 liters	" "	"	contain	0.5 " " "
100 cc.	" "	"	"	0.025 " " "
20 cc.	" "	"	"	0.005 " " "

and so forth, for any volume of solution taken.

(If great accuracy is desired, the solution is measured by weight instead of volume, since weight does not change with temperature and can be more accurately measured.)

Having supposedly used 20.0 cc. of this 0.25 *M*-NaOH in titrating the 50 cc. sample of sulfuric acid solution, we can now say that 0.005 mole of NaOH was used. Since, from the equation, we see that 2 moles of NaOH neutralize 1 mole of  $\text{H}_2\text{SO}_4$ , evidently 0.005 mole of NaOH neutralize 0.0025 mole of  $\text{H}_2\text{SO}_4$ , which is the amount present in the sample. If we want this amount in grams we simply take  $0.0025 \times 98$  g. If we wish to know the molal concentration of the acid, *i.e.*, the number of moles per liter, we see that since 50.0 cc. of the acid solution contain 0.0025 mole of  $\text{H}_2\text{SO}_4$ , 1000 cc. or 1 liter would contain  $\frac{1000}{50} \times 0.0025$ , or 0.05 mole; hence it is 0.05 *M*- $\text{H}_2\text{SO}_4$ . This calculation is obviously simpler than the one involving grams, which necessitated the use of atomic weights.

**4. The Equivalent: Normal Concentration.** It is very convenient, in titration, to have various solutions of the same neutralizing power. Although it is true that solutions of such acids as HCl and  $\text{HNO}_3$  of the same molal concen-

tration may be used interchangeably in titrating bases, solutions of molal  $\text{HCl}$  and molal  $\text{H}_2\text{SO}_4$ , for example, could not be used indiscriminately, since 1 mole of  $\text{H}_2\text{SO}_4$  has twice the power that 1 mole of  $\text{HCl}$  has to neutralize alkali. Similarly, while 10 cc. of 0.1  $M$ - $\text{HCl}$  would neutralize 10 cc. of 0.1  $M$ - $\text{NaOH}$ , it would neutralize only 5 cc. of 0.1  $M$ - $\text{Ba}(\text{OH})_2$ . Since, in titrating acids and bases, we are interested in the hydrogen of the acid and the hydroxyl of the base, the simplest basis for making and using such solutions is the amount of acid hydrogen and basic hydroxyl in a liter of the solution. Solutions of  $\text{NaOH}$  and  $\text{Ba}(\text{OH})_2$  would have the same neutralizing power if equal volumes contained, not 1 mole of each, but 1 mole and  $\frac{1}{2}$  mole, respectively. The amounts of acids and bases to be dissolved in equal volumes of solution are the amounts which, in the particular reactions involved, will yield 1 g. of acid hydrogen and 17 g. of basic hydroxyl, respectively. This amount is called an **equivalent**, and concentration expressed in equivalents is called **normal concentration** and denoted by the letter  $N$ , in the same way that molal concentration is indicated by  $M$ . Thus 2  $N$ - $\text{H}_2\text{SO}_4$  denotes 2 equivalents of this acid per liter; 0.5  $N$ - $\text{KOH}$  denotes 0.5 equivalent of  $\text{KOH}$  per liter. Obviously, whenever the acid and base contain one acid hydrogen atom and one hydroxyl group in the molecule, the mole and equivalent are the same, and so molal and normal concentrations for such acids and bases are the same.

5. The previous example can now be reconsidered in the simpler units. We found that 20.0 cc. of 0.25  $M$ - $\text{NaOH}$  neutralized 50.0 cc. of  $\text{H}_2\text{SO}_4$  solution of unknown concentration. In terms of true acid and alkaline equivalence, or neutralizing power, it is evident that the  $\text{H}_2\text{SO}_4$  solution is less concentrated than the  $\text{NaOH}$  in the ratio 2 to 5, since the corresponding volumes are in the ratio of 5 to 2. The concentration of the  $\text{NaOH}$  is 0.25  $N$ , as well as 0.25  $M$ , since 1 mole is 1 equivalent in this case. The concentration

of the  $\text{H}_2\text{SO}_4$  is therefore  $\frac{2}{5} \times 0.25$  or 0.1 equivalent per liter, which is written 0.1  $N\text{-H}_2\text{SO}_4$ . This calculation is simpler than the one using molal concentration, as the equation need not be used, and the concentrations can be directly compared instead of calculating the moles present in each volume used. It may be made to yield the same results as the other, for 1 equivalent of  $\text{H}_2\text{SO}_4$  is 0.5 mole and 49 g.; hence a solution which is 0.1  $N\text{-H}_2\text{SO}_4$  is 0.05  $M\text{-H}_2\text{SO}_4$  or contains 4.9 g. per liter.

6. If the use of equivalents seems harder to the student than the use of moles or grams, he should psychoanalyze himself. The use of grams corresponds to the ordinary grocery store in which a price list is required to convert pounds to cents. Using moles is like a "grocceteria" in which all commodities are in packages worth 25¢, 50¢, 75¢ or \$1.00. The clerk would not need to know as much arithmetic. A still less educated clerk could get along, however, if every package were worth just \$1.00. He would be very stupid, indeed, if he should allow himself to worry over the different sizes, weights and shapes of the packages.

7. **Summary.** By way of summary it may be stated that any kind of problem involved in titrating acids and bases may be solved by understanding the three following factors and utilizing them in the connection demanded by the problem:

First, **the number of equivalents and the number of grams per mole of substance**, as indicated by the formula; *e.g.*,  $\text{Ca}(\text{OH})_2$  denotes 1 mole, 2 equivalents, 74 g.

Second, **the meaning of the symbols expressing concentration**; *e.g.*, 0.01  $M\text{-Ca}(\text{OH})_2$  denotes a solution of 0.01 mole (hence, by the first step, 0.02 equivalent or 0.74 g.) of  $\text{Ca}(\text{OH})_2$  in a liter.

Third, **the relation between the amount of acid and base used**, which is given by the equation, if amounts are expressed in moles or grams, or without the necessity of considering the equation if equivalents are used, since 1

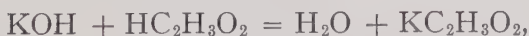
equivalent of any acid neutralizes 1 equivalent of any base, by the definition of the term equivalent.

Any student who has succeeded in being admitted to college surely has enough intelligence to get these matters clear and straight at this stage. One should not flounder and fail for lack of determination and persistence.

8. *Examples:* What is (1) the molal concentration and (2) the normal concentration when 7.4 g. of  $\text{Ca}(\text{OH})_2$  is in 2 liters of solution? 1 mole of  $\text{Ca}(\text{OH})_2$  is 2 equivalents, and weighs 74 g.; hence 7.4 g. is 0.1 mole and 0.2 equivalent. Since this is dissolved in 2 liters, 1 liter would contain 0.05 mole or 0.1 equivalent, so that the solution would be 0.05 molal or 0.1 normal, expressed briefly as 0.05 *M*- $\text{Ca}(\text{OH})_2$  and 0.1 *N*- $\text{Ca}(\text{OH})_2$ , respectively.

9. How many cc. of 0.2 *N*-HCl will be required to neutralize 40.0 cc. of 0.5 *N*-NaOH? By 0.5 *N*-NaOH we mean 0.5 equivalent of NaOH in 1 liter of solution; hence 40.0 cc. of it, which is 0.040 liter, will contain  $0.040 \times 0.5$ , or 0.02 equivalent of NaOH. Since 1 equivalent of any acid neutralizes 1 equivalent of any base, the amount of acid neutralized by 0.02 equivalent of NaOH is 0.02 equivalent. Since 0.2 *N*-HCl means 0.2 equivalent of it per liter of solution, to get 0.02 equivalent we would have to take 0.1 liter, or 100 cc.

10. It was found that the acetic acid in 10 cc. of vinegar was neutralized by 14.0 cc. of 0.5 *M*-KOH solution. How many grams of acetic acid were in 100 cc. of the vinegar? The formula of acetic acid is  $\text{HC}_2\text{H}_3\text{O}_2$ , and only one of the hydrogen atoms in the molecule has acid properties. By 0.5 *M*-KOH we mean a solution containing 0.5 mole of KOH per liter. Since 14 cc. is 0.014 liter, this volume of solution will contain 0.014 of 0.5 mole, or 0.007 mole of KOH. By writing the equation,



we see that 1 mole of the acid neutralizes 1 mole of the base, so that 0.007 mole of the base will be neutralized by 0.007



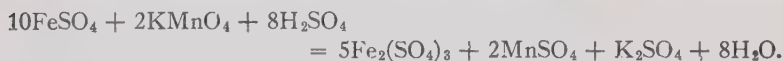
mole of the acid, which is the amount present in 10 cc. of vinegar. Since 1 mole of acetic acid weighs 60 g., 0.007 mole weighs 0.42 g. Since this amount is contained in 10 cc. of vinegar, 100 cc. would contain 4.2 g.

11. If 0.654 g. of zinc is completely dissolved in 100 cc. of 0.5  $M$ - $H_2SO_4$ , what will be the concentration of the acid after the reaction, in terms of: (a) moles per liter, (b) equivalents per liter? The atomic weight of zinc is 65.4, so that 0.654 g. is 0.01 gram-atom of zinc. From the equation for the reaction,



we see that 1 gram-atom of zinc will use up 1 mole of acid; hence, 0.01 gram-atom of zinc would use up 0.01 mole of the acid. Now 1 liter of 0.5  $M$ - $H_2SO_4$  contains 0.05 mole and 100 cc. would contain 0.5 mole. The zinc used up 0.01 mole of this, leaving 0.04 mole of  $H_2SO_4$  in 100 cc., which corresponds to 0.4 mole per liter. Since 1 mole of  $H_2SO_4 = 2$  equivalents, 0.4 mole = 0.8 equivalent and the solution may be called 0.8 normal.

12. **Titration Involving Other Types of Reaction.** It will be seen from the last example above that solutions of known concentration may be used to measure amounts of material in other reactions besides those where acids and bases neutralize each other. The speed with which volumes of solutions can be measured in titrations, makes the former preferable wherever speed is desired. When neutralization of acids and bases does not take place, some other means of indicating the end-point of the reaction is necessary. Where a highly colored substance disappears in the reaction, this may be used to indicate when the exact amount required has been added. Any excess makes itself evident by reason of the color. One such substance frequently used is potassium permanganate,  $KMnO_4$ , a substance with a deep purplish red color, which is a very strong oxidizing agent. As an example of the type of reaction now being considered, let us determine how much iron is in an ore, 1.016 g. of which, when dissolved in acid so as to give a solution containing  $FeSO_4$ , required 45.0 cc. of 0.05  $M$ - $KMnO_4$  to change the  $FeSO_4$  to  $Fe_2(SO_4)_3$ , according to the equation,





The actual amount of  $\text{KMnO}_4$  used is evidently 0.045 of 0.05 mole or 0.00225 mole. According to the equation 2 moles of  $\text{KMnO}_4$  react with 10 moles of  $\text{FeSO}_4$ , so that 0.00225 mole of  $\text{KMnO}_4$  would react with  $5 \times 0.00225$  mole or 0.01125 mole of  $\text{FeSO}_4$ . Now 0.01125 mole of  $\text{FeSO}_4$  contains 0.01125 gram-atom of iron, and since 1 gram-atom of iron is 55.8 g., 0.01125 gram-atom would weigh  $0.01125 \times 55.8$  g., or 0.626 g. Since, finally, this amount of iron was found from 1.016 g. of the ore, the iron is 61.7 per cent of the ore.

**13. Standardizing Solutions.** In making solutions of known concentration for titration we must start with some substance that can be weighed, such as benzoic acid,  $\text{HC}_7\text{H}_5\text{O}_2$  (only one of the hydrogen atoms has acid properties), or sodium carbonate,  $\text{Na}_2\text{CO}_3$ . If it were desired to make 0.05  $M$ - $\text{H}_2\text{SO}_4$ , which contains 0.05 mole or 4.9 g. of  $\text{H}_2\text{SO}_4$  per liter, we would make up a quantity of the solution a little more concentrated than 0.05  $M$  by dissolving about 3 cc. of concentrated acid (density 1.8) in a liter of water. We would next determine accurately the concentration of acid in this solution by titrating a known weight of  $\text{Na}_2\text{CO}_3$ . Suppose that it takes 43.0 cc. of our solution to react with 0.248 g. of  $\text{Na}_2\text{CO}_3$ , according to the equation



Since 1 mole of sodium carbonate reacts with 1 mole of the acid, and since 0.248 g. of  $\text{Na}_2\text{CO}_3$  is 0.00234 mole, the amount of  $\text{H}_2\text{SO}_4$  is also 0.00234 mole, and as this is dissolved in 43.0 cc. the amount in one liter is  $\frac{1000}{43} \times 0.00234$  mole, or 0.0545 mole. This solution may be used in titrations just as it is, or by diluting with the right amount of water the concentration may be adjusted to exactly 0.05 molal. Since 0.05 mole per liter is the same as 0.0545 mole in 1090 cc., if water is added to a liter of the 0.0545 molal solution until the volume becomes 1090 cc., then the concentration of the resulting solution is 0.05 molal, as desired. From this an alkaline solution of desired concentration may then be made up by a similar process.

Chemists are, however, prone to take unnecessary pains to adjust their standard solutions to concentrations expressed by simple numbers. By the aid of a slide rule it is just as easy to calculate the results of titrations where the acid is 0.0545  $M$  as it is when it is exactly 0.05  $M$ .

## EXERCISES

1. Write equations expressing the neutralization of sodium hydroxide with hydrochloric acid; sodium hydroxide with sulfuric acid; calcium hydroxide with nitric acid; barium hydroxide with sulfuric acid.

2. Write under each substance involved in the above equation the number of moles, grams and equivalents represented.

3. How many grams are there in 1 equivalent of each of the following substances:  $\text{KOH}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{Al}(\text{OH})_3$ ? From your answers state how many grams of aluminum hydroxide and of sulfuric acid would combine to form aluminum sulfate.

4. How many moles of sulfuric acid will be neutralized by 4 equivalents of sodium hydroxide? *Ans.* 2 moles.

5. If 0.98 g. of sulfuric acid is in 1 liter of solution, what is (a) the molal concentration? (b) the normal concentration?

*Ans.* (a) 0.01 *M*; (b) 0.02 *N*.

6. When 3.7 g. of calcium hydroxide are in 5 liters of solution, what is (a) the molal concentration? (b) the normal concentration?

*Ans.* (a) 0.01 *M*; (b) 0.02 *N*.

7. (a) How many equivalents of barium hydroxide are in 200 cc. of 0.1 normal solution? (b) How many moles? (c) How many equivalents of hydrochloric acid could this solution neutralize? (d) How many grams?

*Ans.* (a) 0.02; (b) 0.01; (c) 0.02; (d) 0.73 g.

8. If 10 cc. of a certain solution of sulfuric acid neutralized 20 cc. of a normal solution of potassium hydroxide, what was the concentration of the former in (a) equivalents per liter; (b) moles per liter; (c) grams per liter?

*Ans.* (a) 2 *N*; (b) 1 *M*; 98 g. per l.

9. If 25 cc. of 0.2 normal acid neutralized some base, how many equivalents of base were there? How many grams of base were there if the base was (a) sodium hydroxide; (b) calcium hydroxide?

*Ans.* 0.005; 0.2 g; 0.185 g.

10. If 10 cc. of *N*/5 ammonium hydroxide neutralizes 20 cc. of sulfuric acid, what was the concentration of the latter?

*Ans.* 0.1 *N*.

11. How many cc. of 0.2 normal acid are necessary to neutralize 25 cc. of 0.5 normal alkali?

*Ans.* 62.5 cc.

12. How many cc. of 0.2 *M*- $\text{HCl}$  will exactly neutralize 0.02 mole of (a)  $\text{KOH}$ ; (b)  $\text{Ba}(\text{OH})_2$ ; each dissolved in 500 cc. of water?

*Ans.* (a) 100; (b) 200.

13. What volume of hydrogen, measured at  $18^\circ \text{C}$ . and 1.02 atm., could be obtained by the action of zinc in excess upon 200 cc. of 0.5 *M*- $\text{H}_2\text{SO}_4$ ?

*Ans.* 2.34 l.

14. What is the equivalent weight of an acid 1.25 g. of which is neutralized by 25 cc. of 0.4 *N*  $\text{Ba}(\text{OH})_2$ ?

*Ans.* 125 g.

15. (a) How many equivalents of oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , are necessary to neutralize 1 equivalent of  $\text{KOH}$ ? (b) How many moles of the former for 1 mole of the latter? (c) How many grams of the former for 1 gram of the latter?

*Ans.* 1 eq.; 0.5 mole; 0.80 g.

16. 11.2 liters of  $H_2$  at  $0^\circ C.$  and 760 mm. react with an excess of  $Cl_2$ . The product is dissolved in water. What is the molal concentration of  $HCl$  in this solution if its final volume is 500 cc.? *Ans. 2 M.*

17. 30 cc. of 0.1  $M$ - $HCl$  are mixed with 100 cc. of 0.05  $M$ - $Ba(OH)_2$  and the resulting solution is evaporated to dryness. (a) What substances are present in the residue? (b) How many moles of each? (c) How many equivalents of each?

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# Chapter VII

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## *Thermochemistry*

1. There are many chemical reactions in which our interest lies ordinarily not in the substances produced but in the heat evolved or absorbed. The burning of fuels is a chemical reaction, but our purpose in burning them is not to produce the carbon dioxide and water that usually result. These substances we take pains to dispose of by means of chimneys and ventilation. Our purpose is rather to obtain the heat or light that accompanies the reaction. In buying fuels, therefore, the important consideration is not the relative cost of the various available fuels but the relative cost of the heat obtained from each. The chemist should therefore know how the heat of such a reaction may be measured and expressed.

Again, in many reactions of importance, a knowledge of whether heat is absorbed or evolved helps to determine the most desirable conditions for carrying it out, as will be explained in Chapter XIV. Also in technical processes, if heat is absorbed during a reaction, this may have to be considered in estimating the cost, since the heat thus absorbed may have to be supplied by means of fuel or electrical energy.

**2. The Calorie.** The unit in which quantity of heat is most frequently expressed is the calorie (abbreviated cal.). This is the amount of heat required to raise the temperature of 1 g. of water  $1^{\circ}\text{C}.$ <sup>1</sup> Since many heats of reaction involve

<sup>1</sup> In very accurate work it is necessary to specify the temperature of the water,

many thousand calories it is also customary to use a larger unit, the kilogram calorie (abbreviated kg. cal.). This is the heat required to raise the temperature of 1 kilogram of water  $1^{\circ}\text{C}$ . Obviously,  $1\text{ kg. cal.} = 1000\text{ cal.}$

**3. Experimental Determination of Heats of Reaction.** The amount of heat involved in a chemical reaction is determined in an apparatus known as a calorimeter. It consists of a vessel holding perhaps a liter of water, provided with a stirrer and a more or less delicate thermometer. This vessel must be well surrounded by some effective heat insulator, so that the temperature of the water within shall be affected only to the least possible extent by the room temperature. This insulation may be furnished by felt, a water jacket, or, by a vacuum jacket, as in a Dewar flask. The reacting substances may be introduced into the calorimeter in various ways. When the heat of solution of a solid is to be measured, the substance may be sealed in a thin glass bulb immersed in water in the calorimeter. After uniform temperature has been reached the bulb is broken and the solid allowed to dissolve. If the reaction is one like the precipitation of an insoluble substance from dilute solutions, or the neutralization of an acid by a base, one liquid may be inclosed in a thin glass vessel, or in one with a valve, and immersed in the other liquid. The liquids may then be mixed at the proper time. If the reaction is one taking place at a high temperature, it may be carried on within a "bomb" immersed in the water of the calorimeter. A small weighed portion of the material under investigation is placed within this bomb, which is then closed and filled through a tube in the top with oxygen under high pressure. It is then placed in the calorimeter and when uniform temperature is attained the combustion is brought about by means of an electrical connection through the lid of the bomb.

The amount of heat liberated by the reaction is measured by the rise in temperature of the calorimeter contents and the heat capacity of the latter. If water alone were involved, the number of calories liberated would be found simply by multiplying the rise in temperature by the weight of the water. Various other substances are present, however, such as the stirrer, the containing vessel, the thermometer, etc., so that their power of absorbing heat compared with that of water must be measured or calculated and added to the weight of the water as the "water equivalent"

for the amount of heat required to produce the same elevation in temperature is not the same at all temperatures. We thus have the "zero calorie," the "15° calorie" and the "mean calorie," which is the average value between  $0^{\circ}\text{C}$ . and  $100^{\circ}\text{C}$ .

It is possible also to express the quantity of heat in terms of other energy units, since the relation between these different kinds of energy is known. A unit frequently used is the joule, which is  $10^7$  ergs, or 1 volt-coulomb.  $1\text{ cal.} = 4.183\text{ joules.}$

of the calorimeter. This may be measured by allowing a reaction evolving a known amount of heat to take place in the calorimeter, or else calculated, by knowing the heat capacities or specific heats, together with the weights, of the various substances in the calorimeter.

#### 4. The Numerical Representation of Heats of Reaction.

In expressing the results of thermochemical measurements it is usual to include in the equation the number of calories evolved or absorbed. The amounts of substances represented by the equation are understood to be expressed in moles. Thus the equation,

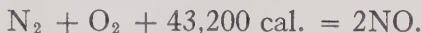


indicates that when 1 mole (12 g.) of carbon burns with 1 mole of oxygen to form 1 mole (44 g.) of carbon dioxide, 96,500 cal. of heat are evolved. This amount of heat is also called the **heat of formation** of carbon dioxide from its elements.

Similarly, the equation



means that when 1 mole (28 g.) of nitrogen reacts with 1 mole (32 g.) of oxygen to form 2 moles (60 g.) of nitric oxide, 43,200 cal. of heat are *absorbed*. This reaction might equally well be written



The ordinary rules of algebra apply to the sign of the heat if the number is thus transposed. Either way of writing the equation signifies that nitrogen, oxygen and heat are all used up in the formation of nitric oxide.

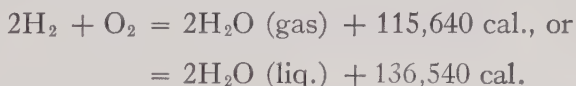
The symbol,  $\Delta H$ , is used to express changes in "heat content" of the system. In the preceding reactions the values of  $\Delta H$  are  $-96,500$  cal. and  $+43,200$  cal., respectively.

The term **exothermic** is often applied to reactions which evolve heat and **endothermic** to those which absorb heat.



It may be mentioned that the former predominate in reactions occurring at ordinary temperatures and the latter in those occurring at very high temperatures, in the electric furnace.

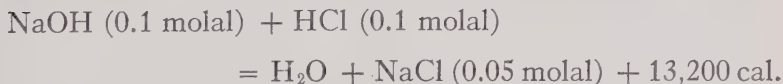
**5. Effect of the State of the Reacting Substances.** The heat of a reaction depends upon the temperature at which it is carried out and upon the state of the substances involved. For example, in the union of hydrogen and oxygen to form water, it makes a difference whether the water produced is at a temperature at which it is liquid or vapor. Since the condensation of steam to liquid takes place with the evolution of heat, it is evident that where the final product is liquid the heat of formation will be greater than when it is a gas. To make this clear we will need to specify in the equation the state of the substance, which we would do in this case as follows:



Or, again, we might find it desirable to express the states of all substances in the equation where ambiguity might otherwise arise, as in the equation,



It makes a difference also whether or not a substance is in solution, and what its concentration is in the solution. We might, therefore, have an equation such as the following:

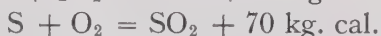


Where the concentration is small and does not need to be specified exactly, it may suffice to use the abbreviation, *aq.*, after the formula of the dissolved substance, which signifies the presence of a large amount of water. (From the Latin *aqua*, water.)

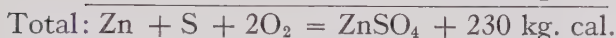
6. In a gaseous reaction in which the number of molecules of gaseous substances changes, the heat will be somewhat different if the reaction is carried out in a closed vessel so that the volume remains constant, from what it will be if the reaction is carried out so as to keep the pressure constant. Since a gas does work in expanding against an external pressure, heat must be absorbed during the expansion in order to maintain the original molecular velocity and hence the original pressure. This behavior finds illustration in the fact that a ball thrown against a yielding surface rebounds with less speed than when thrown against a rigid surface. The heat of a chemical reaction at constant pressure will therefore be greater or less than that of the same reaction at constant volume according as the number of gaseous molecules decreases or increases during the reaction.

**7. Indirect Determination of Heats of Reaction.** In many cases the heat of a reaction cannot be determined directly on account of the difficulty of carrying out the reaction in a calorimeter. In such cases it is usually possible to determine it indirectly. Moreover, even though the reactions may be easily carried out in the calorimeter, it is unnecessary to measure the heats of all, since some may be calculated from others. To do this we use a well-founded law stating that all heats of reaction depend only on the state of the initial or final substances and not upon the steps into which the reaction may be divided. This law is a consequence of the more fundamental law of the conservation of energy, which states that though energy be transformed from one form to another, none of it is ever lost. The different forms of energy include heat, potential energy, or energy of position, kinetic energy, or energy of motion, electrical energy, chemical energy, etc. As an example,  $\text{ZnSO}_4$  might be formed from its elements in either of the following ways:

#### FIRST WAY



## SECOND WAY



The total result in either case is the formation of  $\text{ZnSO}_4$  from  $\text{Zn}$ ,  $\text{S}$  and  $2\text{O}_2$  with the evolution of heat. Our law tells us that the total heat liberated is the same in either case, as shown by the above figures.

As a consequence of this, thermochemical equations may be added or subtracted like any algebraic equations. Suppose that the following heats of reaction have been measured:



and



and we wish to learn the heat of the reaction:



All that is necessary is to eliminate  $\text{CO}_2$  from equations (1) and (2) by multiplying (1) by 2 and subtracting (2) from it, obtaining



or, transposing,



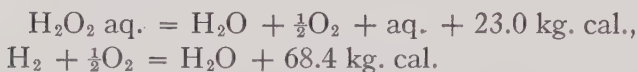
If, on the other hand, we eliminate  $\text{O}_2$  by subtracting (1) from (2), we obtain the equation for a different reaction,



which, since it usually reacts in the reverse direction, we may prefer to write



Again, it is not possible to synthesize  $\text{H}_2\text{O}_2$  aq. from its elements in the calorimeter, but the heat that would be evolved if the reaction were possible may be calculated from the following:



Subtracting the first from the second to eliminate  $\text{H}_2\text{O}$  we obtain:



or, transposing to make the signs positive,



From this we learn that  $\text{H}_2\text{O}_2$  is an exothermic compound, formed *from its elements* with the evolution of heat.

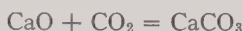
**8. Fuel Value of Foods.** The heat evolved by the combustion of dry food materials in a calorimeter bomb serves for an approximate valuation of their ability to furnish the heat and muscular energy needed by the body. Accordingly, the amount of food materials needed per day can be estimated roughly by the aid of a knowledge of the fuel values of the foods. An adult needs from 2000 to 3500 kg. cal. per day, according to his weight and to the amount of his muscular activity. This makes it possible, for example, to calculate roughly the quantity of food needed, and the relative costs of different foods, which aids in reducing costs of food in the home and in institutions, and furnishes a valuable means of determining the least weight of food necessary for a camping or exploring expedition. It may be of interest to have the few figures given in the following table:

FOODS	APPROXIMATE NUMBER KG. CAL. PER POUND
Starchy foods, cereals, flour, rice, beans, etc. . . . .	1650
Sugar . . . . .	1860
Fats and oils . . . . .	3650
Cheese . . . . .	2000
Chocolate . . . . .	2850
Milk, evaporated, unsweetened . . . . .	800
Milk, condensed, sweetened . . . . .	1500
Dried fruit . . . . .	1300
Fish . . . . .	1000
Meat . . . . .	1600

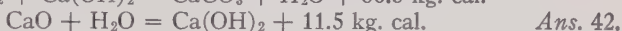
Of course, other considerations must also enter to secure a wholesome, well-balanced diet, but these cannot be discussed here.

### EXERCISES

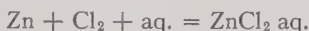
1. What is the distinction between heat and temperature?
2. Calculate the heat of the reaction:



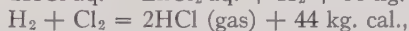
from the following:



3. Calculate the heat of the reaction:



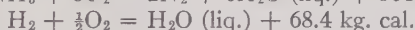
from the following determinations:



4. (a) Calculate the heat of the reaction:



from the following:



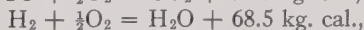
(b) The above figures are for constant pressure; would the heat of formation of  $\text{NH}_3$  be greater or less at constant volume?

5. Given that  $\text{C} + \text{O}_2 = \text{CO}_2 + 96.5 \text{ kg. cal.}$ , and that anthracite coal, considered as 95 per cent carbon, costs \$10 per ton (= 1000 kg.), determine the cost of 1000 kg. cal. from the burning of this coal.

6. Considering "water gas" to consist of  $\text{CO}$  and  $\text{H}_2$  only, as indicated by the equation of its formation,



and given the heats of combustion of  $\text{CO}$  and  $\text{H}_2$ , *i.e.*,



calculate the cost of 1000 kg. cal. from this gas if it costs 90¢ per 1000 cu. ft. (= 28,300 liters) when measured at 20° C. and 1 atm. pressure.

7. If kerosene were pure  $C_{10}H_{22}$ , whose heat of combustion is 1626 kg. cal., and costs 15¢ per gallon (3.781 liters) and has a density of 0.79 g. per cc., calculate the cost of 1000 kg. cal. obtained by burning kerosene.

8. From the table on page 98 make out a "grub-list" for two men on a ten-day walking tour, endeavoring to get the minimum weight consistent with variety and palatability.



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## Chapter VIII

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### *Electrolytic Dissociation*

1. Such a large proportion of the reactions with which we concern ourselves take place in water solution that the behavior of substances dissolved in water is a subject of great importance. We will consider a number of the properties and reactions of substances in aqueous solution, and see that conclusions that may be drawn as to the nature of these solutions are in agreement with the picture in Chapter V.

2. We can better understand the nature of aqueous solutions if we first consider the process of solution in general. In relation to the different types of solids outlined in Chapter V, paragraph 15, a solid composed of distinct molecules is best dissolved by a liquid whose intermolecular forces are of approximately the same strength and nature as those existing in the solid. For example, solid sulfur, containing molecules of  $S_8$ , is readily dissolved by liquid  $CS_2$ . Naphthalene,  $C_{10}H_8$ , is readily dissolved by hexane,  $C_6H_{14}$ . Water is a very poor solvent for these substances because the field of force around a water molecule is different from the fields of force surrounding the molecules just mentioned. The electrons are much more the property of the oxygen than of the hydrogen, hence the water molecule is relatively positive in one part and negative in another. Such a molecule is called an electric dipole and is surrounded by an electrostatic field which is very different in nature from the field of force surrounding a sulfur molecule.

Water is, however, a good solvent for a substance like

sugar, whose molecules contain a number of OH groups, each an electric dipole similar to the water dipole.

Solids of the diamond type are usually nearly insoluble in all solvents. In addition to diamond we may cite as examples quartz and certain of the artificial resins much used today as substitutes for celluloid.

Solids of the salt type are not dissolved by liquids whose molecules are surrounded by symmetrical fields of force

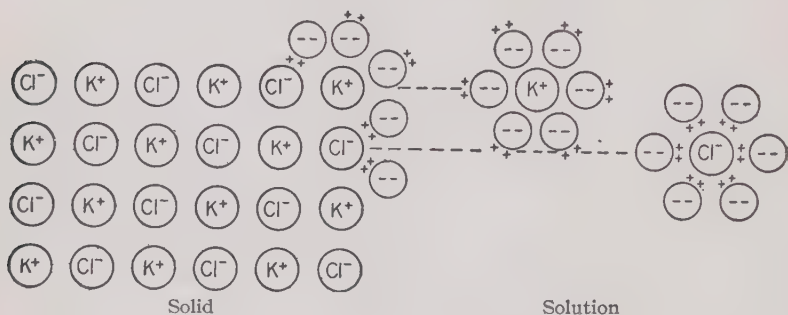


FIG. 1. The process of solution of a salt in water.

such as benzene or gasoline but they are dissolved by liquids whose molecules contain electrostatic dipoles, including water, liquid ammonia and a few others. The process of solution in such a case is easily pictured (Fig. 1). When the water molecule reaches the surface of a salt crystal it tends to orient with its negative part towards the positive potassium atom and its positive part towards the negative chlorine atom. This weakens the force between the charged atoms of the crystal so that, if it is not too strong, the charged atoms may be detached from the crystal and wander off into solution each surrounded by an envelope of oriented water molecules. These charged atoms in solution are but weakly attracted to each other and can move about in the solution more or less independently. They are accordingly called **ions**, from the Greek word meaning to wander.

We will now examine certain properties of salt solutions

to see how they harmonize with this conception regarding their nature.

### 3. Abnormally Great Lowering of the Freezing Point.

It has been pointed out in Chapter III that the molecular weight of substances may be determined by two essentially different methods. One depends upon the property of a mole of any substance in the gaseous form to occupy 22.4 liters at  $0^{\circ}$  C. and 1 atmosphere. The other depends upon the ability of 1 mole of any substance, when dissolved in a given amount of a certain solvent, to exert the same effect upon the escaping tendency of the solvent, as measured by the freezing point, boiling point or vapor pressure. For example, we may define a mole, experimentally, as the number of grams of substance which, in the vapor state at  $0^{\circ}$  C. and 1 atmosphere, will occupy 22.4 liters, or else as the number of grams which, dissolved in 1000 g. of water, will lower the freezing point of the water  $1.86^{\circ}$ . If we determine the effect of various substances on the freezing point of water, we find that a large number of them show concordant behavior. Other substances, including acids, bases and salts, show an abnormally great lowering of the freezing point. This is illustrated in the following table:

TABLE 1

SUBSTANCE	FREEZING POINTS OF 0.1 MOLAL SOLUTIONS
Sugar . . . . .	$-0.188^{\circ}$
Glycerine . . . . .	$-0.186^{\circ}$
Alcohol . . . . .	$-0.184^{\circ}$
NaCl . . . . .	$-0.348^{\circ}$
HCl . . . . .	$-0.356^{\circ}$
KNO <sub>3</sub> . . . . .	$-0.330^{\circ}$
BaCl <sub>2</sub> . . . . .	$-0.478^{\circ}$
Na <sub>2</sub> SO <sub>4</sub> . . . . .	$-0.459^{\circ}$

It will be seen that the first three substances in the table behave as would be expected, but that the others give an abnormally great lowering of the freezing point. There are

two ways of accounting for this abnormality. Either the law of the uniform molal lowering does not hold universally, or else acids, bases and salts dissociate into two or more independent parts when dissolved in water. If this law still holds, then 1 mole of  $\text{NaCl}$ ,  $\text{HCl}$  or  $\text{KNO}_3$ , when dissolved in a large quantity of water, seems to yield nearly 2 moles of dissolved substances, whereas 1 mole of  $\text{BaCl}_2$ , or of  $\text{Na}_2\text{SO}_4$ , seems to yield nearly 3 moles of dissolved substances.

These results harmonize perfectly with the picture of such solutions given above according to which 1 mole of  $\text{KCl}$  in solution exists as 1 mole of  $\text{K}^+$  and 1 mole of  $\text{Cl}^-$ , nearly independent of each other, and each exerting its effect upon the freezing point. This effect is proportional chiefly to the total concentration of ions or molecules in solution and is scarcely influenced by their nature, size or charge. Thus 0.1 mole of  $\text{Br}_2$ ,  $\text{CH}_3\text{OH}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{--}$  would each affect the freezing point to the same extent.

4. The theory that acids, alkalis and salts may be dissociated into charged ions was advanced by Arrhenius in 1881, long before it had been shown that the solid salts also contain charged atoms, and it seemed absurd to many to think of sodium chloride dissolving as atoms of sodium and chlorine, sodium being a metal that reacts violently with water and chlorine a poisonous gas. Such a difficulty is avoided by the realization that an uncharged atom and a charged ion are quite different substances. Thus  $\text{Cu}$  is copper, a reddish metal;  $\text{Cu}^{++}$  or cupric ion, existing in water as a greenish blue substance, is very different from  $\text{Cu}$  in all its properties.

Again,  $\text{H}_2$  is a light, combustible gas, while  $\text{H}^+$  is a substance existing in solution, along with some negative partner, and having a sour taste, etc.

5. **Independent Migration of Ions in Electrolysis.** It has been found that all dissolved substances that give the abnormal effect on the freezing point of water also give

solutions which conduct the electric current, depositing materials at the electrodes, or else dissolving the electrodes. Because of this behavior they are called **electrolytes**. Those conducting very well, the strong acids and alkalis, and most salts, are called **strong electrolytes**.

6. This conductivity is quite in accord with the presence in the solution of charged ions, which must necessarily migrate towards an electrode of opposite charge. The negative electrode, called

the cathode, the one which is receiving electrons from the dynamo or battery, attracts the positive ions, which are accordingly called **cations**, while the positive electrode, the anode, attracts the negative ions, called **anions**. It is possible to detect this migration experimentally. If, for example, we have a U-tube containing, say, dilute copper sulfate in

the bottom, with dilute potassium nitrate carefully superimposed, as shown in Fig. 2*a*, and allow an electric current to pass through the solution for a time, we will find that the blue color characteristic of copper salts travels towards the negative pole, while the sulfate ion travels towards the positive pole, as might be shown by testing layers of solution with a solution of barium chloride. The state of affairs after the passage of current is depicted in the figure at *b*. Whenever electrolysis takes place it is possible to show such independent migration of the two parts of the salt, acid or base, by appropriate experiments similar to the above.

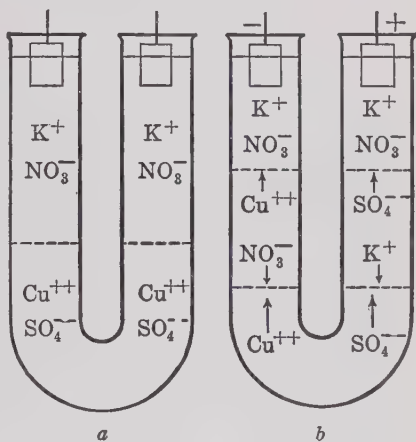
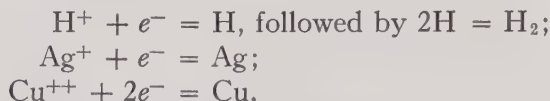


FIG. 2. Independent migration of the ions in electrolysis.

**7. Discharge of the Ions at the Electrodes.** Since a cathode is a metal charged to a certain potential with extra electrons, a positive ion, upon reaching it, may take from it the electron or electrons necessary to change it to a neutral atom. If we represent an electron by the symbol,  $e^-$ , the discharge of ions at a cathode may be represented by equations such as the following:



In some cases an ion may be reduced to an ion of lower charge without being deposited, as  $\text{Fe}^{+++} + e^- = \text{Fe}^{++}$ . To deposit 1 gram-atom of an element,  $6.06 \times 10^{23}$  atoms, requires  $6.06 \times 10^{23}$  electrons for ions with 1 positive charge, such as  $\text{H}^+$  and  $\text{Ag}^+$ , twice as many for ions with two charges, such as  $\text{Cu}^{++}$  and  $\text{Zn}^{++}$ , and so on. The quantity of electricity represented by  $6.06 \times 10^{23}$  electrons is therefore very important and is called a **faraday**, in honor of Michael Faraday, who discovered this electrochemical equivalent. Its magnitude in ordinary electromagnetic units is 96,500 coulombs.<sup>1</sup>

At the anode, where electrons are removed from solution, we may have reactions such as  $\text{Cl}^- = \text{Cl} + e^-$ , followed by  $2\text{Cl} = \text{Cl}_2$ . Frequently the electrons may come from some source other than the anions in solution. Thus, if the anode were made of copper, the electrons removed from the anode would come not from  $\text{Cl}^-$  in solution but from atoms of copper going into solution as  $\text{Cu}^{++}$ . Again, when  $\text{SO}_4^{--}$  is present, although it carries part of the current to the anode it is the water, not the  $\text{SO}_4^{--}$ , which eventually gives up electrons to the anode;  $\text{H}_2\text{O} = 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2e^-$ . (It is sometimes said that the reaction is  $\text{SO}_4^{--} = \text{SO}_3 + \frac{1}{2}\text{O}_2 + 2e^-$ , followed by  $\text{SO}_3 + \text{H}_2\text{O} = 2\text{H}^+ + \text{SO}_4^{--}$ . The

<sup>1</sup> A coulomb is the amount of electricity carried by a current of 1 ampere in 1 second; e.g., 10 amperes flowing for 1 minute would amount to 600 coulombs, and if 1000 coulombs are delivered in 50 seconds, the current strength is 20 amperes.



sum of these two is the reaction previously written, which is the final result in either case. There is probably no evidence that electrons are any more easily removed from  $\text{SO}_4^{--}$  than from  $\text{H}_2\text{O}$ , and the net result is all we are sure of.) In any case Faraday's law holds, and 1 faraday of electricity deposits  $\frac{1}{2}\text{Cl}_2$ ,  $\frac{1}{4}\text{O}_2$ , etc., or dissolves  $\frac{1}{2}\text{Cu}^{++}$ , etc.

8. The following further examples may serve to make the matter clearer. Since 108 g. of silver is 1 gram-atom, deposited by 96,500 coulombs, to deposit 1 g. would require  $\frac{1}{108}$  of 96,500 coulombs, and to deposit 5 g. would require  $\frac{5}{108}$  of 96,500 coulombs, or 4470 coulombs. If this were done by a current of 2 amperes (2 coulombs per second), the time required would be 2235 seconds, or 37 minutes, 35 seconds. However, to deposit 63.6 g. of copper, from ordinary copper salts, 65.4 g. of zinc, etc., requires twice as much electricity, or 2 faradays. Similarly, certain other ions require 3 faradays per gram-ion.

9. It is interesting to note that the requirement of a whole number of faradays of electricity for the discharge of an ion is really a law of simple multiple proportions for electricity and leads to the conclusion that electricity is atomic, and not a "fluid," as it used to be called, just as logically as the law of simple multiple proportions for other matter leads to the conclusion that matter is atomic (cf. Chapter II).

**10. Formulas of Ions.** The formulas of ions are simply related, in many cases, to the number of outer or valence electrons upon the free atom, which, in turn, is correlated with the group of the Periodic System to which an element belongs (cf. Chapter XVII). Thus, the hydrogen atom has one electron and gives  $\text{H}^+$ , the calcium atom has two electrons and gives  $\text{Ca}^{++}$ , etc. The student should learn the formulas of the common ions, such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{Cu}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Al}^{+++}$ ,  $\text{Fe}^{++}$  and  $\text{Fe}^{+++}$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{--}$  and  $\text{CO}_3^{--}$ . When the formula of one ion is known, that of its accompanying ion can be derived; for example, knowing that  $\text{Th}(\text{SO}_4)_2$  must give  $\text{SO}_4^{--}$ , it is

obvious that thorium ion is  $\text{Th}^{++++}$ . Similarly, the formulas of solids or undissociated molecules follow from the ionic charges, such as  $2\text{Al}^{+++} + 3\text{SO}_4^{--} = \text{Al}_2(\text{SO}_4)_3$ ;  $4\text{K}^+ + \text{Fe}(\text{CN})_6^{----} = \text{K}_4\text{Fe}(\text{CN})_6$ ;  $\text{Ca}^{++} + 2\text{H}_2\text{PO}_4^- = \text{Ca}(\text{H}_2\text{PO}_4)_2$ ;  $\text{Ca}^{++} + \text{HPO}_4^{--} = \text{CaHPO}_4$ ;  $3\text{Ca}^{++} + 2\text{PO}_4^{---} = \text{Ca}_3(\text{PO}_4)_2$ .

**11. The Properties of Dilute Aqueous Solutions of Strong Electrolytes Are the Sum of Independent Sets of Properties, Hence Independent Substances Are Present.** It is found that all of the properties of dilute solutions of strong electrolytes are the sum of independent sets of properties belonging to the different kinds of ions present. For example, the colors of salts of a colored with a colorless constituent may be different when the salts are in the solid state showing that the latter are close enough to the former to modify their properties, but the color becomes the same when the substance is dissolved in a large amount of water. Solid  $\text{CuCl}_2$ ,  $\text{CuBr}_2$  and  $\text{Cu}(\text{NO}_3)_2$  are colored green, brown and blue, respectively, but in dilute aqueous solution all assume the same greenish blue color. Since we recognize substances by their properties, we conclude that we have in solution the same substance. Again, the electrical conductivity, refractive index, density, etc., of these solutions depend only on the ions present, and not upon the substances giving the ions. If, say, 0.1 mole of  $\text{NaCl}$  and 0.1 mole of  $\text{KNO}_3$  are dissolved together in a liter of water, the properties of the solution are the same as if the solution were made from 0.1 mole of  $\text{KCl}$  and 0.1 mole of  $\text{NaNO}_3$  dissolved in the same amount of water.

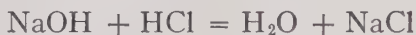
Most striking of all, perhaps, are the chemical reactions. It is not possible to predict the properties of gaseous  $\text{HCl}$  from the properties of hydrogen and those of chlorine, but it is possible to predict the properties of a dilute aqueous solution of  $\text{HCl}$  from the properties common to all other acids, on the one hand, and those common to all soluble chlorides on the other hand. The hydrogen ion in this solu-

tion reacts in the same way and has the same properties as the hydrogen ion obtained from any other acid, as explained in Chapter V. It affects indicators in the same way, it reacts with carbonates, dissolves zinc, tastes sour, just as it always does unless the other ion present exerts some complicating effect on these tests. The chloride ion gives precipitates with the same reagents, such as  $\text{AgNO}_3$  or  $\text{HgNO}_3$  solutions, as are obtained from all other chloride electrolytes. Knowing the properties of chloride ion, as obtained from some chloride, and knowing the properties of a cation, say barium ion, we can predict the properties of dilute solutions of barium chloride, without the aid of direct experiment. This makes it possible to simplify enormously the labor of learning the chemical reactions of electrolytes upon each other. It is necessary only to know the reactions given by the important ions in order to predict the reactions of the enormous number of electrolytes which might be obtained by combinations of these ions. Instead of remembering the action of a large number of sulfates individually upon all soluble barium salts, it suffices to remember that barium ion,  $\text{Ba}^{++}$ , reacts with sulfate ion,  $\text{SO}_4^{--}$ , to give a very insoluble white precipitate of barium sulfate,  $\text{BaSO}_4$ . Such generalizations cannot be made with any degree of assurance with substances that are un-ionized. Alcohol and phenol (carbolic acid) both contain the hydroxyl group (OH), their formulas being  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{C}_6\text{H}_5\text{OH}$ , respectively, but these are not appreciably ionized, and when dissolved in water react very differently, having no set of properties in common. Again, it is not correct to conclude that silver nitrate is a "test for chlorine," as is sometimes stated. Chloroform,  $\text{CHCl}_3$ , will give no such test unless it is heated with silver nitrate for a long time. A solution of potassium chlorate gives no precipitate with silver ion,  $\text{Ag}^+$ , because, although it contains chlorine, it yields no chloride ion,  $\text{Cl}^-$ , but, instead, chlorate ion,  $\text{ClO}_3^-$ .

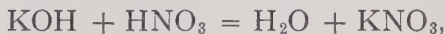
The value of the ionic theory is very great in reducing

equations to their simplest terms and focusing the attention on the essential reactions taking place.

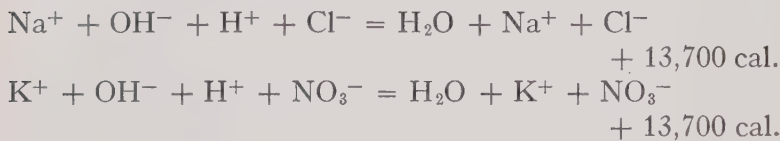
**12. Heats of Reaction in Dilute Solutions of Strong Electrolytes Depend on the Reacting Ions Only.** Heats of reaction between ions in dilute solution are independent of the nature of any other ions present. This is not true for substances not in solution. Solid NaOH and solid KOH do not give the same heat of neutralization with concentrated sulfuric or nitric acid, but when both acid and base are dilute, the amount of heat liberated is always the same, 13,700 calories per equivalent. Since the heat liberated is the same, the reaction liberating it is likely to be the same, and the ionic theory indicates that this should be the case. Instead of writing



and



for the reactions in dilute solution, which would lead us to expect different heats of reaction, we should, according to previous evidence, write



The ionic form of the equations indicates that nothing happens to anything except  $\text{H}^+$  and  $\text{OH}^-$ , which unite to form  $\text{H}_2\text{O}$ ; the other ions, being unaffected, may be canceled from the equation, leaving simply



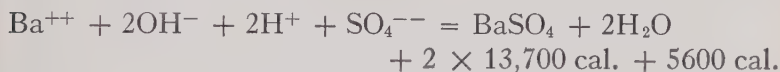
as the fundamental and only reaction in both cases.

The same would apply to precipitations. Any soluble barium salt would give the same heat effect per mole with

any soluble sulfate, since, no matter what other ions are present in the solution, the essential reaction is



If, however,  $\text{Ba}(\text{OH})_2$  and  $\text{H}_2\text{SO}_4$  solutions be used, the heat of reaction would, of course, be no longer the same as above, for then we would have occurring simultaneously two independent reactions, each with its own heat effect, and the ionic equation



shows that nothing should be canceled out.

**13. Degree of Ionization of Strong Electrolytes.** In very dilute solutions, the ions of strong electrolytes are so far apart as to be without influence on each other, but as concentration increases, electrostatic attractions and repulsions come into play, each positive ion tending to surround itself with negative ions, and *vice versa*. This attraction restricts their independence and prevents them from exerting their full individual effects. For example, they suffer a drag as they move in opposite directions while conducting an electric current, as shown in Table 2, which gives the current that would be carried by a mole of KCl at  $18^\circ \text{C}$ . between parallel electrodes 1 cm. apart when diluted by different volumes of water. The limiting conductivity in very dilute solution is evidently about 128, but this is greatly reduced as higher concentrations are reached. The effect of ions on the freezing point is likewise additive only at extremely low concentrations. If a salt gives two ions per mole, the ratio of the freezing point lowering to the concentration should be  $2 \times 1.86^\circ = 3.72$  (cf. paragraph 3). This is closely approached by 0.001 *M*-KCl, as seen in Table 2, but becomes less at higher concentrations.

TABLE 2  
EFFECTS OF IONIC INTERACTION FOR KCl

Concentration moles per 1000 g. of water	0.0002	0.001	0.01	0.1	1
Conductivity divided by concentration	127.9	127.1	122.2	113.7	98.1
Freezing point lowering divided by concentration	—	3.65°	3.61°	3.45°	3.25°



There are other factors that may contribute to these deviations beside the one mentioned above. One of these may be the repulsions suffered by the ions when they happen to come very close to each other; another may be their varying degrees of hydration. In many cases, also, a given pair of ions may temporarily unite to form a molecule. This union is strong in the case of the weak acids and bases and a few salts, and is appreciable in the case of many salts. Even such a strong acid as nitric shows evidence of the presence of  $\text{HNO}_3$  molecules in concentrated solutions. The weak salts mentioned below, in paragraph 15, represent cases of incomplete dissociation. In some cases intermediate ions are formed, as  $\text{Pb}^{++} + \text{Cl}^- = \text{PbCl}^+$ , and  $\text{PbCl}_2 + \text{Cl}^- = \text{PbCl}_3^-$ .

The various formulas connecting the concentrations of the ions with the properties of their solutions all require modification to take into account the several kinds of interaction. Students who pursue this subject further into the realm of quantitative relationships will encounter factors called activity coefficients, which correct the ionic concentrations so as to allow for the variations here discussed. However, the qualitative reasoning called for in this book will yield sufficiently accurate results if we treat strong acids and bases and nearly all salts as completely ionized, the ions having effects proportional to their concentration.

**14. Weak Acids and Bases Are Less Ionized Than Strong Acids and Bases in Solutions of the Same Concentration.** There are some acids and bases which show the properties of hydrogen and hydroxide ions, respectively, to a much less extent than do strong acids and bases in solutions of the same concentration. Solutions of  $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , at the same concentration, say 0.01 normal, would have about the same sour taste, but 0.01 normal acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ , would not taste nearly so sour. The first three acids would show almost identical colors with an indicator like methyl violet, sensitive to that degree of acidity, but it would require approximately normal acetic acid to show the same color. The same weakness on the part of acetic acid is shown in power to conduct current. While, therefore, the properties of acetic acid indicate that it yields hydrogen ion in water, they also indicate that only a little of the hydrogen of the acid is ionized. Again, while the effect of acetic acid on the freezing



point of water is greater than that of an un-ionized substance like sugar, it is not double the latter, as is approximately the case with an acid like hydrochloric acid. Its heat of neutralization is no longer 13,700 cal., as with a strong acid, but has a different value, and includes the heat of dissociation of the acid during its neutralization.

TABLE 3

APPROXIMATE CONCENTRATION OF  $H^+$  IN SOLUTIONS OF VARIOUS ACIDS

MOLES OF ACID DISSOLVED PER LITER		1	0.1	0.01
Hydrochloric . . .	HCl	1	0.1	0.01
Nitric . . . . .	HNO <sub>3</sub>	1	0.1	0.01
Bisulfate ion (NaHSO <sub>4</sub> soln.)	HSO <sub>4</sub> <sup>-</sup>	0.2	0.04	0.008
Acetic . . . . .	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	0.004	0.0013	0.0004
Carbonic . . . .	H <sub>2</sub> CO <sub>3</sub> (CO <sub>2</sub> in water)	—	0.0002	0.00006
Hydrosulfuric . .	H <sub>2</sub> S	—	0.0001	0.00003

There are a number of such weak acids, including carbonic acid, H<sub>2</sub>CO<sub>3</sub>, boric acid, H<sub>3</sub>BO<sub>3</sub>, hydrogen sulfide (hydrosulfuric acid), H<sub>2</sub>S, silicic acid, H<sub>2</sub>SiO<sub>3</sub> (also many poly-silicic acids), nitrous acid, HNO<sub>2</sub>, arsenous acid, H<sub>3</sub>AsO<sub>3</sub>, arsenic acid, H<sub>3</sub>AsO<sub>4</sub>, sulfurous acid, H<sub>2</sub>SO<sub>3</sub>, and hydrocyanic acid, HCN, hypochlorous acid, HClO, etc. Table 3 gives the concentration of  $H^+$  in solutions of four weak acids compared with two strong acids, and indicates clearly the different extent of the ionization. The **degree of ionization** is the fraction, or per cent of the total electrolyte present, which has broken down into ions. For example, the figures for acetic acid show that if 0.1 mole of acetic acid is dissolved in 1 liter, 0.0013 mole of  $H^+$  is liberated; since every  $H^+$  produced requires one molecule of HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> to split up, 0.0013 moles of the acid have dissociated, which is  $0.0013 \div 0.1$  or 1.3 per cent of the acid taken. It is to be noted that as a weak acid is diluted the degree of ionization increases although the concentration of  $H^+$  diminishes.

The most important weak base ordinarily encountered is

ammonium hydroxide,  $\text{NH}_4\text{OH}$ . It is this weakness which makes it useful in cleansing, for although it does not yield enough free hydroxide ion to be injurious in washing, yet, if the little it does yield is used up, more can dissociate, the undissociated portion acting as a sort of reserve for hydroxide ion.

**15. Weak Salts.** Most salts are highly ionized when in solution, even though they be salts of weak acids or bases, like sodium acetate or ammonium chloride. There are, however, a few exceptions, including lead acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , the iodide of cadmium,  $\text{CdI}_2$ , mercuric chloride,  $\text{HgCl}_2$ , mercuric cyanide,  $\text{Hg}(\text{CN})_2$ , and ferric sulfocyanate,  $\text{Fe}(\text{CNS})_3$ . These salts are poor electrolytes, and their reactions in solution show the presence of relatively few ions. For example, all ordinary soluble chlorides give a precipitate of lead chloride,  $\text{PbCl}_2$ , on the addition of lead ion to their solutions. With mercuric chloride, however, no precipitate is obtained, indicating that there is less chloride ion in a concentrated solution of mercuric chloride than in a saturated solution of the rather insoluble lead chloride. If, however, silver ion is taken, a precipitate is formed, for silver chloride,  $\text{AgCl}$ , is much less soluble than lead chloride, and  $\text{HgCl}_2$  yields enough chloride ion to precipitate it.

**16. Ionization of Weak Polybasic Acids in Steps.** It is found that the two or more hydrogen atoms in the molecule of a polybasic acid, like  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{S}$  or  $\text{H}_3\text{PO}_4$ , tend to dissociate with unequal readiness into ions. While the first hydrogen atom of  $\text{H}_2\text{CO}_3$  is but slightly ionized, it is possible to neutralize it with  $\text{OH}^-$ , forming water and  $\text{HCO}_3^-$ , before the neutralization of the second hydrogen atom, in the  $\text{HCO}_3^-$ , begins. This explains the ease with which it is possible to form acid salts in such cases. The first atom of hydrogen in  $\text{H}_3\text{PO}_4$  ionizes readily, corresponding to a moderately strong acid; the second ionizes from  $\text{H}_2\text{PO}_4^-$  with much less ease, so that the ion  $\text{H}_2\text{PO}_4^-$  is a rather

weak acid, while the third is hard to neutralize,  $\text{HPO}_4^{--}$  being a very weak acid. Conversely, when hydrogen ion,  $\text{H}^+$ , is added to an ion like  $\text{PO}_4^{---}$  it is taken up very completely at first until the latter is converted into  $\text{HPO}_4^{--}$ , then less completely until  $\text{H}_2\text{PO}_4^-$  is formed, and then only a little to form  $\text{H}_3\text{PO}_4$ . It takes, likewise, a smaller concentration of  $\text{H}^+$  to change  $\text{CO}_3^{--}$  to  $\text{HCO}_3^-$  than it does to change  $\text{HCO}_3^-$  to  $\text{H}_2\text{CO}_3$ . Even  $\text{H}_2\text{SO}_4$  forms some  $\text{HSO}_4^-$  in more concentrated solutions.

**17. Ionization in Other Solvents Than Water.** Water is the chief solvent in which we are interested, but there are others which can dissolve electrolytes with ionization. The most important of these are liquid ammonia and the alcohols. Ionization in all other solvents that have been investigated is less than in water, and seems to be roughly proportional to the dielectric constant of the liquid. The following values for the dielectric constants for several liquids are of interest in this connection:

Water . . . . .	80	Ammonia . . . . .	16
Methyl (wood) alcohol . .	31	Chloroform . . . . .	5
Ethyl alcohol . . . . .	26	Ether . . . . .	4
Acetone . . . . .	22		

**18. Ionization of Fused Salts.** Fused salts appear to be highly ionized, conducting the electric current very readily. This corresponds to the fact that melting a salt like  $\text{NaCl}$  merely releases the charged atoms,  $\text{Na}^+$  and  $\text{Cl}^-$ , already present, held in fixed positions in the solid state, but free to move in the molten state towards charged electrodes. On account of this high conductivity many substances are obtained industrially by the electrolysis of fused salts rather than of aqueous solutions. This is the case especially with metals like sodium, calcium and aluminum, where, instead of the desired metal, the hydrogen from the water would be deposited at the cathode. Sodium and calcium are obtained, along with chlorine gas, by the electrolysis of their fused chlorides. Aluminum, used at the present time in such large amounts, is obtained by the electrolysis of  $\text{Al}_2\text{O}_3$  dissolved in fused cryolite,  $\text{Na}_3\text{AlF}_6$ .

**19. Ionization of Water.** Water itself is very slightly ionized. The purest water that can be prepared has a very

slight conductivity due to  $H^+$  and  $OH^-$ . Knowing the conductivities of these ions in more concentrated solution, as we do from measurements with acids and bases, it is possible to calculate the concentration of these ions in water to be approximately  $10^{-7}$  molal<sup>1</sup> at ordinary temperatures. This corresponds to 0.1 milligram of  $H^+$  and 1.7 milligrams of  $OH^-$  per ton of water. Other methods of measurement confirm these figures.

20. The method of calculation from conductivity is illustrated by the following scheme.

SOLUTION MEASURED	IONS PRESENT	CONDUCTIVITY AT 18°
0.001 <i>M</i> -HCl	0.001 <i>M</i> - $H^+$ + 0.001 <i>M</i> - $Cl^-$	$377 \times 10^{-6}$
0.001 <i>M</i> -KOH	0.001 <i>M</i> - $K^+$ + 0.001 <i>M</i> - $OH^-$	$234 \times 10^{-6}$
	Sum	$611 \times 10^{-6}$
0.001 <i>M</i> -KCl	0.001 <i>M</i> - $K^+$ + 0.001 <i>M</i> - $Cl^-$	$127 \times 10^{-6}$
	0.001 <i>M</i> - $H^+$ + 0.001 <i>M</i> - $OH^-$ if they could exist together	$484 \times 10^{-6}$
Pure water	$x$ molal $H^+$ + $OH^-$	$0.042 \times 10^{-6}$

Conductivity is proportional to concentration, therefore

$$\frac{484}{.042} = \frac{10^{-3}}{x}, \text{ or } x = 0.9 \times 10^{-7}.$$

### EXERCISES

1. How would you define acid, base, salt, in terms of the ionic theory?
2. Summarize in writing the evidence in favor of the theory of electrolytic dissociation.
3. State in writing all the evidence you have learned, showing that a solution of acetic acid is much less ionized than one of hydrochloric acid of the same concentration.
4. Divide the following substances into two lists, one for those slightly ionized in water, the other for those highly ionized: ammonium hydroxide, ammonium chloride, hydrochloric acid, sodium acetate, carbonic acid, sodium chloride, mercuric chloride.

<sup>1</sup> This number is equivalent to writing  $\frac{1}{10^7}$  or  $\frac{1}{10,000,000}$ .

5. Write the formulas of all the salts that can be formed from the following ions:  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Al}^{+++}$ ,  $\text{SO}_4^{--}$ ,  $\text{Cl}^-$ .

6. What are the properties of  $\text{H}_2$  and  $\text{H}^+$ ? How might each one be converted into the other?

7. What are the properties of the following substances:  $\text{Cu}$ ;  $\text{Cu}^{++}$ ;  $\text{Ag}$ ;  $\text{Ag}^+$ ;  $\text{Cl}_2$ ;  $\text{Cl}^-$ ?

8. Describe some of the properties of the dilute aqueous solutions of the following:  $\text{HCl}$ ;  $\text{KNO}_3$ ;  $\text{H}_2\text{SO}_4$ ;  $\text{Na}_2\text{SO}_4$ ;  $\text{KCl}$ ;  $\text{CuCl}_2$ ;  $\text{CuSO}_4$ .

9. How does the evidence obtained from the heat of neutralization support the ionic theory?

10. Write the principal reaction occurring when (a)  $\text{NaCl}$  dissolves in water; (b) a solution of sodium sulfate is evaporated; (c) concentrated  $\text{HCl}$  solution is warmed.

11. In writing the following equations represent all substances by formulas indicating that they are mainly ionized or un-ionized, as the case may be: a solution of acetic acid is neutralized by one of sodium hydroxide; silver nitrate and potassium chloride solutions are mixed, giving a precipitate of silver chloride; dilute hydrochloric acid acts on a solution of sodium carbonate, giving  $\text{CO}_2$  gas, water and sodium chloride solution; zinc is put into a solution of copper sulfate, giving a precipitate of metallic copper; concentrated sulfuric acid acts on solid sodium chloride, giving hydrogen chloride gas and solid sodium sulfate; mercuric chloride solution is treated with hydrogen sulfide gas, giving a precipitate of mercuric sulfide, etc.

12. What is the concentration of  $\text{OH}^-$  in (a) equivalents per liter, and (b) grams per liter, when 0.37 g. of  $\text{Ca}(\text{OH})_2$  is dissolved in 500 cc.?

13. A solution of  $\text{HAc}$  is found to give the same color with methyl violet as a certain solution of  $\text{HCl}$ . Which would neutralize the larger proportion of base? Explain.

14. Define or explain the following terms: ion, electrolyte, degree of ionization, faraday, electron.

15. What is the degree of ionization of a weak monacid base if the concentration of the  $\text{OH}^-$  in a 0.5 normal solution is 0.002 normal?

*Ans.* 0.4%.

16. (a) What is the concentration of  $\text{H}^+$  in a 2 molal solution of acetic acid if it is 0.006 ionized? (b) What is the concentration of  $\text{Ac}^-$  (i.e.,  $\text{C}_2\text{H}_3\text{O}_2^-$ )? (c) Of the un-ionized  $\text{HAc}$ ?

*Ans.* (a) (b) 0.012 M, (c) 1.988 M.

17. How many (a) faradays, (b) coulombs are required to deposit 1 g. of each of the following ions at the appropriate electrode; and (c) how long will it take using a current of 1 ampere: (1)  $\text{H}^+$ , (2)  $\text{Ni}^{++}$ , (3)  $\text{Cl}^-$ , (4)  $\text{Al}^{+++}$ ?

*Ans.* (2) (a) 0.034, (b) 3290, (c) 55 min.

18. Arrange the following in order of their freezing points, starting

with the highest: (a) 1 *N*-HCl; (b) 0.1 *N*-HCl; (c) 1 *N*-HAc; (d) 0.1 *M*-sugar; (e) 0.1 *M*-H<sub>2</sub>SO<sub>4</sub>; (f) water. *Ans. fdbeca.*

19. 0.1-g. atom of Zn is added to 0.05 moles of HCl in 500 cc. H<sub>2</sub>O. (a) What substances are present in the final solution? (b) What is the quantity of each in moles? (c) What is the concentration of each in moles per liter? *Ans. (c) 0.05 M-Zn<sup>++</sup>; 0.1 M-Cl<sup>-</sup>.*

20. State what electron changes occur when (1) an electric current is passed through a copper wire; (2) metallic zinc dissolves in acid; (3) chlorine gas acts upon metallic sodium.

21. Outline experiments to show whether glutaric acid is stronger or weaker than succinic acid.



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# Chapter IX

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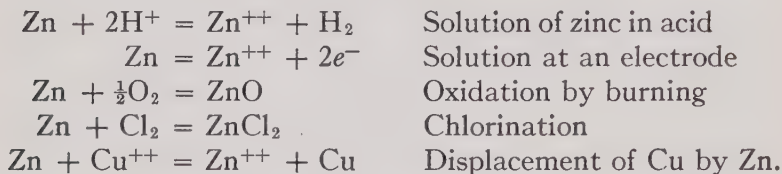
## *Combining Proportions*

**1. Ionic Charges.** The proportions in which ions combine to form neutral substances are readily derived from their charges. Conversely, when the formula of an ionizing substance is known, together with that of one of its ions, the formula of the other ion is readily obtained. Examples have been given in Chapter VIII, paragraph 10.

The ionic charges, as explained in Chapter V, depend on the number of electrons an atom can gain or lose. The elements, H, Li, Na, K, have but one outer electron to lose, hence, on combining with other elements, take a charge of + 1. The elements Be, Mg, Ca, Sr, Ba, have two outer electrons and give the ions  $\text{Be}^{++}$ ,  $\text{Mg}^{++}$ , etc. The atoms F, Cl, Br, I, with seven outer electrons, add one to complete an octet, becoming  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ .

**2. Oxidation Number.** A substance may be insoluble in water and fail to give in that way a direct indication of the number of electrons each atom has lost or gained; nevertheless, we may feel confidence in the conclusions from more indirect evidence. For example,  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  are insoluble in water but they dissolve in  $\text{H}^+$  as follows:  $\text{FeO} + 2\text{H}^+ = \text{Fe}^{++} + \text{H}_2\text{O}$ ;  $\text{Fe}_2\text{O}_3 + 6\text{H}^+ = 2\text{Fe}^{+++} + 3\text{H}_2\text{O}$ . They can also be formed from  $\text{Fe}^{++}$  and  $\text{Fe}^{+++}$  as follows:  $\text{Fe}^{++} + 2\text{OH}^- = \text{Fe}(\text{OH})_2 = \text{FeO} + \text{H}_2\text{O}$ ;  $2\text{Fe}^{+++} + 6\text{OH}^- = 2\text{Fe}(\text{OH})_3 = \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$ . Now  $\text{H}^+$  is a substance which becomes  $\text{H}_2$  when it acquires electrons at a cathode and  $\text{OH}^-$  becomes  $\text{O}_2$  and  $\text{H}_2\text{O}$  when it loses electrons at

an anode; hence we conclude that the iron in FeO and Fe<sub>2</sub>O<sub>3</sub>, respectively, has the same number of electrons as in Fe<sup>++</sup> and Fe<sup>+++</sup>. We shall call the charge which an element appears to have its **oxidation number or state**. The term **valence** has been much used for this purpose, but since it is often used also for coördination number, to be explained later (paragraph 9) its use in either sense leads to confusion, hence has been avoided in this book. The reason for using the word oxidation may be illustrated by comparing the following reactions:

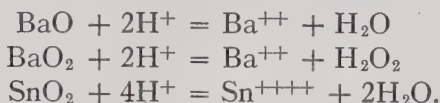


Each of these processes involves essentially the removal of the two electrons from each zinc atom. Although the third reaction only is literally oxidation, the term is extended in a figurative sense to include them all. Accordingly, the oxidation number of zinc has been increased in each case from 0 to + 2.

3. The reverse process, a gain in electrons, or decrease in oxidation number, is designated by an obviously general term, **reduction**. In the above reactions involving Zn, the H<sup>+</sup>, O<sub>2</sub>, Cl<sub>2</sub> and Cu<sup>++</sup> have been reduced, their oxidation numbers having changed as follows: H<sup>+</sup>, + 1 to 0; O<sub>2</sub>, 0 to - 2; Cl<sub>2</sub>, 0 to - 1; Cu<sup>++</sup>, + 2 to 0.

4. The oxidation number can be assigned with little ambiguity to elements that always lose the same number of electrons, such as H, Na, K, Mg, Ca, Al; however, there are exceptions to ordinary behavior. Thus Li and H<sub>2</sub> react to form LiH, which fuses to give a conducting melt from which H<sub>2</sub> separates at the anode, or pole from which electrons are being removed. The hydrogen atom has the unusual charge, or oxidation number - 1, and the reaction is evidently

$\text{H}^- = \frac{1}{2}\text{H}_2 + e^-$ . Again, the oxygen in most of its compounds has an oxidation number of  $-2$ , having gained 2 electrons per atom to complete the octet, as we might expect. It is otherwise, however, in a class of compounds called peroxides, including  $\text{H}_2\text{O}_2$ ,  $\text{BaO}_2$ ,  $\text{Na}_2\text{O}_2$ . Evidence for this is seen in the following contrasting reactions:



It is evident that the oxidation numbers of Ba and O cannot be the same in both  $\text{BaO}$  and  $\text{BaO}_2$ ; however, both give the ordinary  $\text{Ba}^{++}$  on reaction with acid, hence it is the oxygen which is unusual. In  $\text{SnO}_2$ , on the other hand, it is the tin that is different. Evidently in both  $\text{BaO}_2$  and  $\text{H}_2\text{O}_2$  the oxidation number of the two atoms of oxygen together is  $-2$ . Now we cannot tell without more evidence whether the electrons are distributed evenly between the two atoms, so that each is  $-1$ , or whether they are unsymmetrical, *e.g.*, 0 and  $-2$ . For most purposes, fortunately, it makes no difference, hence we may regard  $-1$  as the formal oxidation number.

5. Compounds whose atoms are held together by electron-pair bonds range gradually from those in which the electron-pair is equally shared to those in which the pair is largely displaced towards one of the atoms. Such gradations are shown in Table 2, Chapter V. To assign the bonding electrons entirely to the more negative atom is evidently rather arbitrary except where the substance is ionic as with  $\text{MgO}$ . It is useful, nevertheless, to make such an arbitrary assignment, for it enables us, first, to classify the compounds of an element according to their oxidation numbers and, second, to balance equations for reactions involving oxidation and reduction by a simple formal procedure (*cf.* Chapter XVIII).

6. Thus,  $\text{SF}_6$ ,  $\text{SO}_2$ ,  $\text{SO}_4^{--}$  and  $\text{H}_2\text{SO}_4$  are classed together

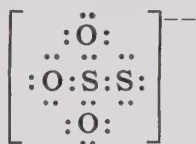
as compounds containing sulfur with an oxidation number of + 6; with  $\text{SCl}_4$ ,  $\text{SO}_2$  and  $\text{SO}_3^{--}$  it is + 4; while in  $\text{H}_2\text{S}$ ,  $\text{SH}^-$  and  $\text{ZnS}$  it is - 2. These oxidation numbers are assigned by aid of the knowledge that oxygen has a very strong tendency to add 2 electrons in all its compounds except the peroxides; chlorine is usually - 1, hydrogen is usually + 1, and zinc + 2. Furthermore, the changes involving no change in oxidation number are simpler than those which do.

7. Compounds of arsenic are readily classified according to oxidation number in the accompanying table.

TABLE 1  
OXIDATION NUMBERS OF ARSENIC

0	+ 3	+ 5	- 3
As	$\text{AsCl}_3$	$\text{AsF}_5$	$\text{H}_3\text{As}$
0	+ 3, 3(- 1)	+ 5, 5(- 1)	3(+ 1), - 3
	$\text{As}_2\text{O}_3$	$\text{As}_2\text{O}_5$	$\text{Mg}_3\text{As}_2$
	2(+ 3), 3(- 2)	2(+ 5), 5(- 2)	3(+ 2), 2(- 3)
	$\text{AsO}_2^-$	$\text{AsO}_3^-$	
	+ 3, 2(- 2)	+ 5, 3(- 2)	

8. An interesting case is presented by the sulfur in sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$ , the "hyposulfite of soda" of photography. The thiosulfate ion probably has the structure,



like that of  $\text{SO}_4^{--}$ . This ion can decompose to give off the extra sulfur as free sulfur, whose atoms are  $:\ddot{\text{S}}:$ , or as sulfide ion,  $:\ddot{\text{S}}:^-$ , depending upon the reagents used. We can accordingly say that the inner and outer sulfur atoms are respectively either + 4 and 0, or + 6 and - 2, depending upon which behavior we are considering. Either assump-

tion, however, would serve to give a formal means of balancing an equation, as will be seen in Chapter XV.

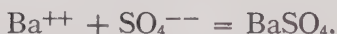
9. There is another kind of combining value called **coördination number**, and sometimes, also, valence, **that expresses the number of atoms, irrespective of charge, that can group themselves around the atom in question.** In sulfate ion and thiosulfate ion the coördination number of the central atom is 4. In  $\text{SF}_6$  it is 6. Silver, with a charge of  $+1$ , has a coördination number of 2 in the compounds,  $\text{Ag}(\text{NH}_3)_2^+$  and  $\text{Ag}(\text{CN})_2^-$ . Platinum, in  $\text{PtCl}_6^{--}$ , has a coördination number of 6, although it may be regarded as containing  $\text{Pt}^{++++}$ .

With carbon compounds the bond to other atoms is nearly or quite non-polar, that is, the electrons are shared by both atoms, and it is usually inappropriate to say that one atom has gained and another lost electrons. The coördination number, which is usually 4, here becomes the significant number in determining combining power, and is called the valence, without distinction between positive and negative values (cf. Chapter XVIII).

10. **Writing Equations.** In connection with chemical equations it is important to realize that the mere writing of the equation confers no obligation upon the substance involved to behave as indicated by the equation. The obligation is rather upon the one who writes the equation to endeavor to make it correspond to an actual or possible reality. A complete justification of an equation would require the experimental determination both of the substances produced, their formulas and their relative amounts. A knowledge of oxidation numbers aids in writing the formulas of substances likely to be formed and also in fixing the numbers of atoms and molecules necessary to make an equation "balance," a necessary feature of an equation.

11. Equations involving the mere splitting of molecules into ions or *vice versa* are easily balanced with due regard to electric neutrality. For example, if a solution of  $\text{Al}_2(\text{SO}_4)_3$ ,

which contains  $\text{Al}^{+++}$  and  $\text{SO}_4^{--}$ , is mixed with one of  $\text{BaCl}_2$ , which contains  $\text{Ba}^{++}$  and  $2\text{Cl}^-$ , the  $\text{SO}_4^{--}$  unites with the  $\text{Ba}^{++}$  to form a precipitate of  $\text{BaSO}_4$ ; hence we write simply,



The  $\text{Al}^{+++}$  and  $\text{Cl}^-$  which are present have not reacted, so that they need not be put into the equation any more than the water, the containing vessel or other necessary feature of the reaction.

12. Let us consider, next, the reaction between aluminum and  $\text{Fe}_3\text{O}_4$  to form aluminum oxide and iron. To be absolutely certain of the formula of the aluminum oxide produced we would have to determine it by analysis. We do not, however, find aluminum compounds in which the oxidation number of aluminum is other than 3, as we see it in  $\text{AlCl}_3$ . This would lead us to anticipate that the oxide formed would be  $\text{Al}_2\text{O}_3$ , which is correct. Accordingly, we have Al and  $\text{Fe}_3\text{O}_4$  giving  $\text{Al}_2\text{O}_3$  and Fe. We must next adjust the number of molecules so that there will be the same number of atoms of each element on each side of the equation. It is obvious that we must take  $3\text{Fe}_3\text{O}_4$  to get an integral number, 4, of  $\text{Al}_2\text{O}_3$  molecules. Adjusting the number of atoms of Al and Fe, we have as the equation



It is always desirable to check the equation written by comparing the number of atoms of each element on each side of the equation. They should, of course, be equal.

### EXERCISES

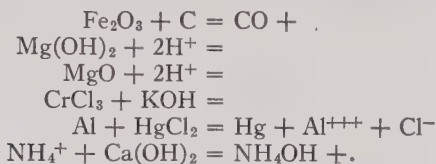
1. What is the probable oxidation number of each radical and element in each of the following compounds:  $\text{CuSO}_4$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{PbCO}_3$ ,  $\text{CrCl}_3$ ,  $\text{MgO}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{CuS}$ ,  $\text{FeCO}_3$ ,  $\text{KClO}_3$ ,  $\text{K}_2\text{CrO}_4$ ,  $\text{Fe}(\text{OH})_2$ ?

2. Write the formulas of a number of other compounds that might be formed from the constituent parts of the above compounds (omitting the atoms within the radicals).



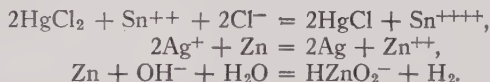
3. Explain the terms: oxidation number, coördination number, oxidation, reduction.

4. Complete and balance the following incomplete equations:



5. Classify according to the state of arsenic the following arsenic compounds:  $\text{AsCl}_3$ ,  $\text{As}_2\text{O}_3$ ,  $\text{As}_2\text{O}_5$ ,  $\text{As}_2\text{S}_5$ ,  $\text{NaAsS}_2$  (consider the number of S to be  $-2$ ),  $\text{H}_3\text{As}$ ,  $\text{H}_3\text{AsO}_4$ ,  $\text{Ag}_3\text{As}$ .

6. In each of the following reactions determine what elements are oxidized and what reduced:



7. Explain why both positive and negative oxidation numbers are used.

8. Is As oxidized or reduced when it is changed from (1)  $\text{AsCl}_3$  to  $\text{As}_2\text{O}_5$ , (2)  $\text{H}_3\text{As}$  to  $\text{As}_2\text{O}_3$ , (3)  $\text{As}_2\text{O}_5$  to  $\text{AsO}_4^{---}$ ?

9. Classify the following substances according to the state of the sulfur in them:  $\text{H}_2\text{S}$ ;  $\text{SO}_2$ ;  $\text{HSO}_3^-$ ;  $\text{SH}^-$ ; S;  $\text{SO}_4^{--}$ ;  $\text{SO}_3$ ;  $\text{Na}_2\text{S}_2\text{O}_3$ ;  $\text{SCl}_4$ ;  $\text{ZnS}$ .

10. Classify the following substances according to the state of the iron in them:  $\text{Fe}_2(\text{SO}_4)_3$ ;  $\text{FeS}$ ; Fe;  $\text{FeSO}_4$ ;  $\text{FeCl}_3$ ;  $\text{Fe}(\text{CN})_6^{----}$ ;  $\text{Fe}_2\text{O}_3$ ;  $\text{Fe}(\text{OH})_2$ ;  $\text{KFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ;  $\text{BaFeO}_4$ .

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# Chapter X

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## *Chemical Nomenclature*

1. The common names of most familiar substances, given before the development of chemistry as a science, usually give no clue to their composition. However, as the number of known substances has increased it has become necessary to use names which are based upon some system. The multiplication of terms such as "oil of vitriol" (which is not an oil), "copperas" (which contains no copper), "Glauber's salt," "cream of tartar," "muriatic acid," etc., would place an almost impossible task upon the memory if it were extended to the hundred thousand or more known substances. To avoid such a situation as is found in mineralogy, where the terms give little clue to the composition of the substance, chemists have evolved a nomenclature which is based upon the elements composing the compound. This nomenclature has the advantage of being almost international, so far as the European languages are concerned.

2. **Names of the Elements.** The only generalization possible in the nomenclature of the elements is in regard to the names of the metals. The effort has been to give the Latin neuter suffix, *-um*, to the names of metals, as illustrated by potassium, magnesium, platinum. Where the element was commonly known before the introduction of this systematic nomenclature we may have still surviving the common name without this suffix, as with iron, silver, copper, gold. In such cases the Latin name, from which the symbol is derived, may, however, often be used to designate

compounds. For example, instead of copper sulfate we may say cupric sulfate, from the Latin *cuprum*. The reason for this use of the Latin name will become apparent later.

The group  $\text{NH}_4$ , which gives compounds analogous to those of the metal potassium, is called ammonium.

**3. The Most Positive Element Named First.** It is customary to give the name of the most metallic or positive element first in naming the compound (corresponding to the order used in writing the formula), as is seen in the names of aluminum oxide, sodium chloride, copper sulfide, magnesium sulfate, potassium nitrate, hydrogen fluoride, carbon dioxide, etc.

**4. Binary Compounds Designated by Suffix *-ide*.** When the compound consists of but two elements it is customary to add the suffix *-ide* to the name of the second or less metallic element in naming the compound. Thus all compounds of oxygen with a single more positive element are called oxides, those of chlorine are called chlorides, those of phosphorus, phosphides, those of carbon, carbides, etc.

In a few cases this suffix is used where the compound contains more than two elements because of the existence of certain groups acting much like a single element. For example, the cyanide group,  $\text{CN}$ , acts very much like the halogens; hence  $\text{KCN}$  is called potassium cyanide, by analogy with  $\text{KCl}$ , potassium chloride.

**5. Designation of Compounds Where the Positive Element May Show Different Oxidation Numbers.** As was pointed out in Chapter IX, there are many elements showing more than one oxidation state in their compounds, so that the simple naming of the constituents as above leaves an ambiguity as to which of the possible compounds is meant. There are, for example, two chlorides, oxides, etc., of mercury, iron, tin, lead, copper, etc., so that it is not sufficient, in these cases, to speak of mercury chloride, iron chloride, tin oxide, copper sulfide, etc. In most cases the positive elements exhibit but two oxidation states,

and it is possible to distinguish their two series of compounds by adding the suffixes *-ous* and *-ic* to the name of the positive element, signifying the lower and higher valences respectively. Accordingly, we designate  $\text{HgCl}$  as mercurous chloride and  $\text{HgCl}_2$  as mercuric chloride;  $\text{As}_2\text{O}_3$  as arsenous oxide, and  $\text{As}_2\text{O}_5$  as arsenic oxide. In many cases the common English name of the element does not lend itself to this usage, as with the elements iron, copper, tin, lead. In such instances the Latin name of the element is used, so that we have  $\text{FeCl}_2$ , ferrous chloride, and  $\text{FeCl}_3$ , ferric chloride,  $\text{Cu}_2\text{O}$ , cuprous oxide, and  $\text{CuO}$ , cupric oxide,  $\text{SnS}$ , stannous sulfide, and  $\text{SnS}_2$ , stannic sulfide.

6. Another way of distinguishing between different compounds of the same element is by the use of the Latin and Greek numeral prefixes to the names of the elements. These prefixes, up to eight, are as follows:

	1	2	3	4	5	6	7	8
Latin	<i>Uni-</i>	<i>Bi-</i>	<i>Ter-</i>	<i>Quadri-</i>	<i>Quinque-</i>	<i>Sexa-</i>	<i>Septi-</i>	<i>Octa-</i>
Greek	<i>Mono-</i>	<i>Di-</i>	<i>Tri-</i>	<i>Tetra-</i>	<i>Penta-</i>	<i>Hexa-</i>	<i>Hepta-</i>	<i>Octo-</i>

To these we may add the Latin *sesqui-*, meaning one and a half. By the use of these prefixes we can often designate the compound with less ambiguity than by means of the suffixes *-ous* and *-ic*, especially when more than two compounds exist. As examples of the use of these prefixes we may mention  $\text{CO}$ , carbon monoxide, and  $\text{CO}_2$ , carbon dioxide;  $\text{CS}_2$ , called both carbon bisulfide and carbon disulfide;  $\text{PCl}_3$ , phosphorus trichloride, and  $\text{PCl}_5$ , phosphorus pentachloride;  $\text{Cr}_2\text{O}_3$ , chromium sesquioxide, and  $\text{CrO}_3$ , chromium trioxide;  $\text{Sb}_2\text{S}_3$ , (di)antimony trisulfide (antimonous sulfide) and  $\text{Sb}_2\text{S}_5$ , (di)antimony pentasulfide (antimonic sulfide).

7. The prefix *per-* is used in binary compounds chiefly to denote oxides in which the oxygen is related to the oxygen in hydrogen peroxide,  $\text{H}_2\text{O}_2$ , with an average number of  $-1$ . The most important besides hydrogen peroxide are barium peroxide,  $\text{BaO}_2$ , and sodium peroxide,  $\text{Na}_2\text{O}_2$ . It is

doubtless wise to use the term only with oxides of this type, though this is by no means a uniform practice.

A compound like  $\text{Fe}_3\text{O}_4$ , which is doubtless composed of  $\text{FeO}$ , ferrous oxide, and  $\text{Fe}_2\text{O}_3$ , ferric oxide, may be designated as ferrous-ferric oxide, though it is usually referred to as "magnetic iron oxide." Similarly,  $\text{Pb}_3\text{O}_4$  is usually known by its commercial name "red lead."

**8. Binary Acids.** Acids consisting of hydrogen and one other element are designated by the prefix *hydro-* and the suffix *-ic*, like  $\text{HCl}$ , hydrochloric acid;  $\text{HN}_3$ , hydronitric acid;  $\text{H}_2\text{S}$ , hydrosulfuric acid.

**9. Oxy-acids and Salts.** Certain elements capable of assuming more than one oxidation state form two or more acids containing oxygen. In such cases the significance of *-ous* and *-ic* in distinguishing higher and lower oxidation state is similar to that used with binary compounds. We have  $\text{H}_2\text{SO}_3$ , sulfurous acid, and  $\text{H}_2\text{SO}_4$ , sulfuric acid;  $\text{HCrO}_2$ , chromous acid, and  $\text{H}_2\text{CrO}_4$ , chromic acid;  $\text{H}_3\text{AsO}_3$ , arsenous acid, and  $\text{H}_3\text{AsO}_4$ , arsenic acid; and  $\text{HNO}_2$ , nitrous acid, and  $\text{HNO}_3$ , nitric acid. When more than two oxygen acids of the same elements exist, the prefixes *hypo-* and *per-* are used, as illustrated in the following table, which shows at the same time the salt designations corresponding to the different types of acid, using the acids of chlorine for illustration:

ACID		CORRESPONDING SALT	
$\text{HCl}$	Hydrochloric	$\text{KCl}$	Potassium chloride
$\text{HClO}$	Hypochlorous	$\text{KClO}$	Potassium hypochlorite
$\text{HClO}_2$	Chlorous	$\text{KClO}_2$	Potassium chlorite
$\text{HClO}_3$	Chloric	$\text{KClO}_3$	Potassium chlorate
$\text{HClO}_4$	Perchloric	$\text{KClO}_4$	Potassium perchlorate

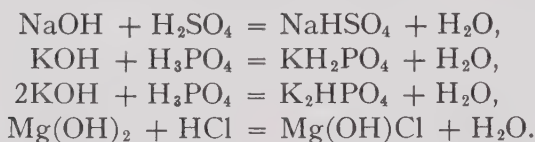
**10. Sulfo-acids and Salts.** There are many cases where sulfur replaces oxygen in salts, though the corresponding acids are not capable of existing free. These are designated in the same way as the oxy-salts, using the prefix *sulf(o)-*, or sometimes *thio-*. We have  $\text{KSbO}_2$ , potassium antimonite,

and  $\text{KSbS}_2$ , potassium sulfantimonite;  $\text{KSbO}_3$ , potassium antimonate and  $\text{KSbS}_3$ , potassium sulfantimonate;  $\text{KCNO}$ , potassium cyanate, and  $\text{KCNS}$ , potassium thiocyanate.

In the case of  $\text{Na}_2\text{S}_2\text{O}_3$ , which seems to be a sulfate with one oxygen atom replaced by a sulfur atom, the name thiosulfate is given.

**11. Complex Halogen Acids and Salts.** Similar to the oxy- and sulfo-acids we have others containing the halogens, like  $\text{H}_2\text{PtCl}_6$ , chlor-platinic acid, giving salts called chlor-platinates;  $\text{H}_2\text{SiF}_6$ , fluo-silicic acid (cf.  $\text{H}_2\text{SiO}_3$ , silicic acid);  $\text{HAuCl}_2$ , chlor-aurous acid and  $\text{HAuCl}_4$ , chlor-auric acid.

**12. Acid and Basic Salts.** Many acids have more than one replaceable hydrogen atom in the molecule, and many bases have more than one replaceable hydroxyl group in the molecule. Sulfuric acid, for example, is called a  **dibasic acid** on account of its ability to neutralize two hydroxyl groups. Similarly,  $\text{H}_3\text{PO}_4$ , phosphoric acid, is a tribasic acid. On the other hand,  $\text{Mg}(\text{OH})_2$ , magnesium hydroxide, is a  **diacid base** for similar reasons. In such cases it is usually possible to have partial neutralization of either acid or base so as to give either an acid salt or a basic salt. The following equations represent the formation of such salts:



The salts produced in these reactions would be called, respectively, sodium acid (or hydrogen) sulfate, potassium di-hydrogen phosphate, di-potassium hydrogen phosphate and magnesium hydroxy-chloride or basic magnesium chloride.

Sometimes a basic or hydroxy-salt may lose water, becoming an oxy-salt. With bismuth hydroxide, for example,  $\text{Bi}(\text{OH})_3$ , the progressive neutralization with  $\text{HCl}$  would give first  $\text{Bi}(\text{OH})_2\text{Cl}$ , then  $\text{Bi}(\text{OH})\text{Cl}_2$ , finally  $\text{BiCl}_3$ . The first of these loses water, becoming  $\text{BiOCl}$ , a well-known



substance called bismuth oxychloride. In naming these two kinds of basic salts chemists are not always careful to distinguish between an oxy-salt and a hydroxy-salt, but there is some justification in this, on account of the uncertainty existing in many cases as to whether the water present in the precipitate is actually combined or not.

Sometimes this oxy-group plays the part of a radical, existing throughout various metathetical reactions. The radical is then usually designated by the suffix *-yl*, as in  $\text{BiOCl}$ , bismuthyl chloride,  $\text{CrO}_2\text{Cl}$ , chromyl chloride,  $\text{UO}_2\text{Cl}_2$ , uranyl chloride.

Acid salts may likewise lose water, but the possible types of compounds can best be understood in connection with the various types of partially dehydrated acids.

**13. Partially Dehydrated Acids and Their Salts.** If an acid salt like  $\text{KHSO}_4$ , potassium acid sulfate, is heated, it loses water according to the equation



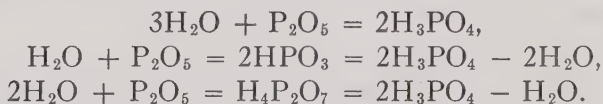
The same result is obtained by adding  $\text{SO}_3$  to  $\text{K}_2\text{SO}_4$ . With reference to its mode of formation this salt is called potassium pyro-sulfate (from the Greek *pyr*, meaning fire). It may also be called potassium bi-sulfate on account of the extra  $\text{SO}_3$  present. This is more evident if the formulas of both the sulfate and the bisulfate are expressed as compounds of acid and basic anhydrides, as was done in Chapter V for many salts, giving  $\text{K}_2\text{O} \cdot \text{SO}_3$ , and  $\text{K}_2\text{O} \cdot 2\text{SO}_3$ , respectively. There are other examples of this type. When acid is added to a chromate, as  $\text{K}_2\text{CrO}_4$ , instead of getting an acid salt,  $\text{KHCrO}_4$ , there results a bichromate, as represented by the equation



There is no great distinction between a bi-salt and an acid salt (in solution it is generally impossible to distinguish

them), so that the former name is applied somewhat indiscriminately. Thus  $\text{NaHCO}_3$ , sodium acid carbonate, is often called sodium bicarbonate, though the real bicarbonate, which would be  $\text{Na}_2\text{C}_2\text{O}_5$ , does not exist. Similarly  $\text{KHSO}_4$  may be called potassium bisulfate. Sometimes it is possible to have still more of the acid anhydride present, as with  $\text{K}_2\text{Cr}_3\text{O}_{10}$  and  $\text{K}_2\text{Cr}_4\text{O}_{13}$ , called potassium trichromate and tetrachromate, respectively, or in general, polychromate (from the Greek *poly*, meaning many). This again becomes most obvious when the formulas are written in terms of the acid and basic anhydrides, giving  $\text{K}_2\text{O} \cdot 3\text{CrO}_3$  and  $\text{K}_2\text{O} \cdot 4\text{CrO}_3$ .

With a tribasic acid like phosphoric acid,  $\text{H}_3\text{PO}_4$ , there exist several partial anhydrides, like  $\text{HPO}_3$  and  $\text{H}_4\text{P}_2\text{O}_7$ . The relations between these acids is best brought out by the equations,



In the first,  $\text{H}_3\text{PO}_4$ , we have the maximum amount of water, and it is called ortho-phosphoric acid (from the Greek *ortho*, meaning straight, direct). The second, meta-phosphoric acid (from the Greek *meta*, meaning after), may be derived by the simple abstraction of water from the ortho-acid. The third is called pyro-phosphoric acid. The application of these terms to several other acids, as in the following table, will make them clearer:

ACIDS	BORIC	SILICIC	PHOSPHORUS	STANNIC
Ortho	$\text{H}_3\text{BO}_3$	$\text{H}_4\text{SiO}_4$	$\text{H}_3\text{PO}_3$	$\text{H}_4\text{SnO}_4$
Meta	$\text{HBO}_2$	$\text{H}_2\text{SiO}_3$	$(\text{HPO}_2)$	$\text{H}_2\text{SnO}_3$
Pyro	$\text{H}_2\text{B}_4\text{O}_7$ (also called tetra-)	(Many poly- silicic acids. $\text{H}_2\text{O} \cdot n\text{SiO}_2$ )	$\text{H}_4\text{P}_2\text{O}_5$	

It is evident that there is no distinction between a pyro-acid and its salts and a poly-acid, and where there are

several it is not customary to use the prefix pyro- with its ambiguous significance, for although there is but one pyrophosphoric acid there are a number of poly-silicic acids, which require such distinguishing terms as di-meta-silicic acid for  $\text{H}_2\text{Si}_2\text{O}_5$ ; tri-meta-silicic acid for  $\text{H}_2\text{Si}_3\text{O}_7$ ; di-ortho-silicic acid for  $\text{H}_4\text{Si}_2\text{O}_6$ , etc. The salts are, of course, designated as for the simpler acids; thus  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$  is di-sodium-di-hydrogen pyro-phosphate,  $\text{Na}_2\text{B}_4\text{O}_7$  (borax) is sodium tetra- (or pyro-) borate,  $\text{K}_2\text{SnO}_3$  is potassium metastannate.

### EXERCISES

1. How should each of the following substances be named:  $\text{CaH}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{PbS}$ ,  $\text{Ni}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_3$ ,  $\text{Hg}_2\text{SO}_4$ ,  $\text{HgSO}_4$ ,  $\text{PbO}$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{CuCO}_3$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{Hg}(\text{NO}_3)_2$ ,  $\text{Hg}(\text{OH})\text{NO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{OH}$ ,  $\text{NH}_4\text{HSO}_4$ ,  $\text{KHNH}_4\text{PO}_4$ ,  $\text{SbCl}_3$ ,  $\text{SbCl}_5$ ,  $\text{SbOCl}$ ,  $\text{NaCl}$ ,  $\text{NaClO}$ ,  $\text{AlCl}_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{NaH}_2\text{AlO}_3$ ,  $\text{NaAlO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{SO}_3$  (cf.  $\text{H}_2\text{SO}_4$ , sulfuric acid),  $\text{NaHSO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_7$ ,  $\text{SO}_3$ ,  $\text{Sb}_2\text{O}_3$ ?

2. Give the names of the following substances: (1)  $\text{ClO}_3^-$ ; (2)  $\text{NaClO}$ ; (3)  $\text{HBr}$ ; (4)  $\text{HClO}_2$ ; (5)  $\text{KIO}_4$ .

3. What facts about the following substances can be concluded from their names: thallium; silver arsenide; thallos chloride; carbon bisulfide; phosphorus pentabromide; nitrogen iodide; cerium; ceric chloride; lead dioxide?

4. Give the formulas of the following substances: (a) oxygen gas; (b) carbonate radical; (c) ammonium hydroxide; (d) cuprous sulfide; (e) aluminum sesquioxide; (f) nitrogen trichloride.

5. If  $\text{H}_3\text{AsO}_4$  is called arsenic acid, what should each of the following be called:  $\text{HAsO}_3$ ,  $\text{H}_3\text{AsO}_3$ ,  $\text{H}_4\text{As}_2\text{O}_7$ ,  $\text{PbHAsO}_4$ ,  $\text{KAsS}_3$ ?

6. If  $\text{K}_2\text{MnO}_4$  is called potassium manganate, what should  $\text{KMnO}_4$  be called?

7. If  $\text{H}_4\text{SnO}_4$  is called ortho-stannic acid, what would you call each of the following:  $\text{H}_2\text{SnO}_2$ ,  $\text{NaHSnO}_3$ ,  $\text{NaHSnO}_2$ ,  $\text{Na}_2\text{SnS}_3$ ?

8. If  $\text{KCNO}$  is the only oxygen salt of its type, what should it be called? (CN is the "cyanide" group.) What should each of the following be called:  $\text{KCNS}$ ,  $\text{HCNO}$ ,  $\text{KCN}$ ,  $\text{HCN}$ ?

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# Chapter XI

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## *The Speed of Chemical Reactions*

**1. The Problem.** The previous chapters have been taken up with various aspects of the nature and composition of substances, and with the representation of substances and their reactions by means of formulas and equations. We are now ready to inquire into the means of controlling chemical reactions so as to realize desirable possibilities or prevent undesirable ones. There are two factors involved in this control, the direction and the speed. For example, at high temperatures the following reaction takes place readily:



The theory to be developed in Chapter XV shows that it should be possible to reverse this reaction at low temperatures and make ammonia from its elements. We find by experiment, however, that the reaction proceeds so slowly at low temperatures as to be utterly useless as a means of making ammonia, and that we must seek some means for its acceleration in order to make it of any practical use. The means of altering the direction of a reaction will be discussed in the following chapters, this one being devoted to the question of speed in reactions where the direction is already assured. Sometimes we may wish to increase the speed of a reaction, as in the cooking of food, and sometimes we may wish to retard an undesirable reaction, such as the rusting of iron or the decay of wood. How may this be done?

**2. Application of the Kinetic Theory.** We have seen, in connection with the behavior of gases and solutions, Chapters III and IV, how fruitful is the kinetic theory of matter. We may apply it with equal success to the problem of controlling the speed of chemical reactions. In order that reactions may take place between different substances their molecules must come together, or collide. We should therefore expect any means of increasing the number (and perhaps the force) of these collisions to be effective in increasing the speed. What means are available for changing the number and speed of these collisions?

**3. Effect of Temperature.** Since the kinetic theory connects the temperature of any body with the velocity of the molecules composing it, one way indicated for increasing the number and also the force of the molecular collisions is to increase the temperature. We find, as a matter of fact, that the effect of increasing the temperature is always to increase the reaction velocity. For reactions occurring within a single phase, *e.g.*, between dissolved or gaseous substances, it is found that the effect of increasing the temperature  $10^{\circ}$  is frequently to increase the speed from two to four times. Where the reaction occurs at the boundary line between two phases, as in dissolving a solid, the effect of temperature is usually somewhat less.

**4.** Chemists constantly make use of the accelerating effect of higher temperature in chemical reactions, and we see it constantly in everyday life. The reactions responsible for the growth of plants, for the decay of dead animal and plant substances, for the souring of milk, are all greatly influenced by the temperature, so that the importance of warmth for growth and of cold storage for preservation is well known to all. The housewife sets her bread to rise in a warm place to hasten the fermentation which produces the carbon dioxide. Those who have lived or camped at high altitudes know of the difficulty of cooking certain foods at the lower temperature at which water boils under such

conditions. The difficulty is sometimes solved by means of "pressure cookers," which hold the steam under pressure, allowing a higher temperature to be reached. Such an apparatus may also be used at ordinary altitudes, resulting in a great saving of fuel when cooking such things as beans or the tougher cuts of meat, for it requires scarcely any more fuel to maintain a temperature of  $120^{\circ}$  than it does to maintain one of  $100^{\circ}$ , although a reaction that requires 5 hours at the latter temperature might be completed in less than 1 hour at the former. In such processes as extracting glue, gelatin and fats, "superheated steam" is used with similar effect. The speed of cooking such a thing as a potato is also increased by cutting it into small pieces, so that all parts of it are quickly brought to the temperature of the boiling water in which it is immersed.

5. The process of hardening steel is an interesting case of retarding a reaction by lowering the temperature. Above  $766^{\circ}$  a steel containing 0.9 per cent carbon consists of a hard, tough variety of iron holding the carbon in solid solution, but below that temperature it tends to change into a heterogeneous mixture, shown in Fig. 5, page 10, of soft iron (like wrought iron) and a hard, brittle iron carbide,  $\text{Fe}_3\text{C}$ , known as cementite. However, this transition requires an appreciable time, and if the steel, heated above  $725^{\circ}$ , is suddenly cooled by quenching in water, so that low temperatures are quickly reached, the tough solid solution may be obtained at ordinary temperatures, where the velocity of the change is practically negligible. This is shown in Fig. 2, page 10. A solution which required 10 seconds for transition at  $766^{\circ}$  to the variety stable at ordinary temperatures would require 300,000 billion years at  $20^{\circ}$  if the reaction velocity were halved for every  $10^{\circ}$  fall in temperature. Hardened steel is thus an unstable substance at ordinary temperatures but we can keep it almost indefinitely by reason of the extreme slowness of its change into the stable variety. If we cool the steel slowly, *i.e.*, anneal it, or if we allow the hardened



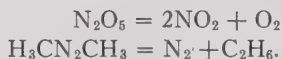
steel to get too warm for a while, as by too rapid grinding or cutting with a tool, it changes into the stable soft mixture, losing its "temper."

6. Many chemical substances are similarly unstable at ordinary temperatures, existing only because the speed at which they decompose is small. In this class are included ozone,  $O_3$ , hydrogen peroxide,  $H_2O_2$ , nitric oxide,  $NO$ , and all explosives. Nitric oxide is stable in the true sense only at the temperature of a very hot electric arc and it can be obtained at ordinary temperatures by a process of rapid cooling similar in principle to the hardening of steel.

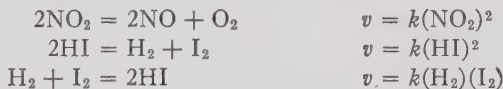
7. **Spontaneous combustion** is the result of the preliminary slow oxidation which many combustible substances undergo in contact with air. Ordinarily the heat of these reactions is liberated so slowly that it has time to be conducted away, so that no perceptible rise in temperature of the oxidizing material takes place. When, however, the material is a poor conductor of heat, like oil-soaked cotton waste, and is in large quantities, so that the heat produced is partly retained, then the rise in temperature causes an increase in the rate of oxidation, with a further gradual rise in temperature, until the temperature of ordinary rapid combustion is attained, and the material bursts into flames.

8. **Effect of Concentration.** Another means of increasing the number of favorable collisions between molecules is to increase the concentration of the reacting substances. The more concentrated a substance is, the more chances there are of its molecules colliding with those of other substances; hence an increase in the concentration of each kind of reacting molecule should increase the speed of reaction. If, for example, two molecules have to collide in order to bring about a certain reaction, then doubling the concentration of either should double the speed of reaction, and doubling the concentration of both should quadruple the speed. Of course, as the reacting substances are used up the speed diminishes.

**9. Numerical Relation between Concentration and Speed.** If  $c_1$ ,  $c_2$ ,  $c_3$  etc., denote the concentrations of the reacting molecules, then the velocity of the reaction,  $v$ , as measured by the rate of disappearance of one of the substances or the formation of another, is proportional to, or equal to a constant times the product of the concentrations of the reacting molecules, *i.e.*,  $v = kc_1c_2c_3$ . . . . If a molecule can decompose without reacting with another the reaction is called **unimolecular** and the rate at which the substance disappears is obviously proportional to its concentration at the moment; *i.e.*,  $v = kc$ , or, if we start with  $A$  moles in  $V$  liters and after a time,  $t$ , the amount decomposed is  $x$ , the amount remaining is  $A - x$  and its concentration is  $(A - x)/V$  and the velocity  $\frac{\Delta x}{\Delta t} = k \frac{A - x}{V}$ . Examples of unimolecular reactions are:



If two molecules must collide, the reaction is **bimolecular**, and  $v = kc_1c_2$ . Examples are:



where the parentheses indicate concentrations of the enclosed substance.

Reactions in which the velocity depends on collisions between three or more molecules are very rare because of the fact that simultaneous collisions between three or more molecules are vastly less frequent than collisions between two molecules. One could convince himself of this by throwing three dice repeatedly and comparing the number of triple sixes with the number of double sixes obtained.

Cases in which the total reaction involves a number of molecules are thus usually split up into two or more steps, the slowest of which determines the rate. For example, the reaction



might appear to be pentamolecular but it is actually trimolecular; experiments show that its velocity is given by  $k(\text{H}^+)(\text{Br}^-)(\text{H}_2\text{O}_2)$ . There appear to be two steps,



The first is slower, hence determines the rate, since  $\text{HBrO}$  can decompose

by (2) only so fast as it is being formed by (1). If (2) were slower, a different rate law would be found.

The determination of the "mechanism" or steps of a reaction is often a difficult matter, but is essential for the understanding and hence the control of reactions. The relative speed of the different steps and their reversibility, and the temporary production of intermediate products all play rôles in fixing rate laws.

**10. Effect of Stirring and of Contact Surface in Reactions Occurring at the Boundaries between Phases.** If a reaction occurs at the boundary between phases, as in the solution of a solid in a liquid, it is evident that stirring would have great effect in bringing fresh reacting molecules to the surface of contact, also in removing the products of reaction from the scene of action. The natural tendency of the molecules to diffuse can thus be greatly aided.

Likewise, contact between the materials in the two phases can be aided by having the contact surface large. For this reason powdered sugar will dissolve more rapidly than granulated or lump sugar.

We may summarize and illustrate the foregoing by stating the conditions for the rapid solution of a metal in acid as follows: high temperature, concentrated acid (unless the salt produced would be thereby rendered insoluble, preventing its diffusion away from the surface of the metal), the use of a strong acid like hydrochloric acid, giving a high concentration of hydrogen ion, instead of a weak acid like acetic acid, giving a small concentration of hydrogen ion (assuming that the metal is a base metal which will be dissolved by hydrogen ion), stirring the solution, and using the metal in rather finely divided condition rather than in large pieces.

An undesirable reaction may, of course, be hindered by the converse of the above means.

**11. Effect of Catalysts.** Many reactions can be accelerated or retarded by the presence of substances which are not themselves permanently used up by the reaction, and which

need be present only in small amount to affect the speed for a large amount of reacting mixture. Such substances are called **catalysts**. One class of catalysts acts by furnishing a surface at which the reacting molecules are condensed and concentrated, causing them to come into more intimate contact. Platinum and palladium act in this way for a number of gas reactions. Hydrogen and oxygen scarcely react at all at ordinary temperatures, but platinum and palladium have the power to absorb these gases, especially the hydrogen, and allow them to react with each other. Under suitable conditions the heat produced by this union may be sufficient to raise the temperature of the metal to a point where it can ignite the remaining gas mixture. Some gas and cigar lighters are constructed on this principle, and when the platinum or palladium is held in the stream of gas mixed with air, or in the escaping vapors of wood alcohol from a wick, the gas or vapor is ignited by the heat generated at first in the catalyst. Platinum finds extensive use in the "contact process" for the manufacture of sulfuric acid. As will be explained in Chapter XIV, the reaction



(sulfuric acid is obtained by dissolving  $\text{SO}_3$  in water) occurs in the desired direction only at lower temperatures, where the reaction proceeds too slowly to be of use. When, however, the gases are passed over platinum at about  $500^\circ \text{C}$ . they react readily, so that the process has supplanted the older "lead-chamber process" to a considerable extent.

12. When platinum is used to catalyze reactions its effectiveness may be increased by increasing the surface as much as possible, exposing atoms at edges and corners of the solid lattice, which, thus relieved of part of the attraction of their neighbors, are able to exert a stronger effect on the adsorbed substance. This is particularly important because of the high cost of platinum. The usual form in which it is used is "platinized asbestos," made by wetting

asbestos fiber with a solution of a platinum salt and then heating it so as to decompose the salt and yield finely divided metallic platinum.

13. The union of nitrogen and hydrogen directly to give ammonia, referred to at the beginning of this chapter, is brought about by the aid of a similar catalyst, iron, to whose aid we owe this important means for the fixation of atmospheric nitrogen and its application as fertilizer.

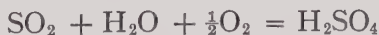
14. Hydrogen peroxide is a very unstable substance, tending to decompose so as to give oxygen and water. This decomposition is aided by the presence of finely divided solids, such as manganese dioxide,  $\text{MnO}_2$ . This oxide likewise catalyzes other reactions where oxygen is evolved, notably



In making oxygen by heating potassium chlorate it is customary to add powdered manganese dioxide, so that the oxygen will be evolved more smoothly and at a lower temperature.

To prevent the decomposition of hydrogen peroxide, besides keeping it dilute and cool, as the kinetic theory would require, a negative or retarding catalyst is frequently added in the form of acetanilid,  $\text{C}_6\text{H}_5\text{NHOC}_2\text{H}_3$ .

15. Many catalysts evidently act as "carriers," by the formation of an intermediate product which then decomposes readily. Such a catalyst is  $\text{NO}$ , as used in the "lead-chamber process" for the manufacture of sulfuric acid. The reaction



does not occur with sufficient speed, but since the reaction

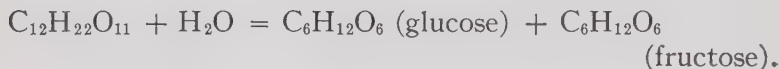


occurs readily in both directions, the oxides of nitrogen make the oxygen available in the following way,



The  $\text{NO}_2$  is regenerated as shown above, so that a little of it suffices for the manufacture of an almost indefinite quantity of sulfuric acid.

16. An interesting reaction is the "inversion" of cane sugar, which consists in its splitting up, with the addition of a molecule of water, into two molecules of simpler sugars, fructose and glucose, containing the same atoms but in different arrangement. The reaction is



The resulting mixture of sugars is often called invert sugar. This reaction is catalyzed by the hydrogen ion of acids and the speed of inversion is proportional to the concentration of hydrogen ion, which doubtless forms an intermediate product. Since the resulting invert sugar does not easily crystallize, it is important, in the refining of sugar, to avoid all acidity of the sugar solutions. When stewed fruit is sweetened the effect of the sugar will be greater if the fruit is sweetened while hot, causing the inversion of the sugar by the acid of the fruit. The altered taste of lemonade that has stood for some hours is due mainly to this inversion of its sugar. It is of interest to note that the sugar in honey is invert sugar. The inversion doubtless takes place in the body of the bee when it is gathered, and prevents subsequent crystallization in the comb.

By a process analogous to the inversion of sugar, starch may be made to take up water, becoming transformed into a mixture of various sugars to which is given the commercial name "glucose." Large quantities of syrup and sugar are made from cornstarch by digestion with acid, which acts as the catalyst.

17. Water is a catalyst for many reactions. Absolutely dry  $\text{CO}$  will not burn. Dry  $\text{AgNO}_3$  and  $\text{HCl}$  dissolved in



ether form no precipitate of  $\text{AgCl}$ . When ordinary  $\text{NH}_4\text{Cl}$  is heated it sublimes, dissociating into  $\text{NH}_3$  and  $\text{HCl}$  gases. If, however, the salt is quite dry, it vaporizes without dissociation.

**18. Enzymes.** An important class of catalysts, known as enzymes, are produced by living organisms and catalyze many reactions. The ptyalin of saliva, whose function is to convert starch into sugar, the diastase of malt, which has a similar action, and the zymase of the yeast plant, which converts certain sugars into alcohol and carbon dioxide, are examples of important enzymes. Similar bodies are thought to play fundamental rôles in the processes of growth and nutrition of plants and animals.

**19. Activation.** The slowness of reactions may be related to the stability of the reacting molecules, indicating that they must first be "opened up" in some way before their atoms can rearrange themselves in new molecules. It requires 103,000 cal. to dissociate a hydrogen molecule; 210,000 cal. to dissociate  $\text{N}_2$ . It is not strange, therefore, that these substances are slow to react at ordinary temperatures. It is not necessary in most cases, however, to split molecules into atoms in order for them to react. It suffices to "activate" them by bombarding them with electrons, by subjecting them to light of appropriate frequency, or by raising their temperature to a value where molecular collisions are sufficiently strong to introduce more energy into the molecule. Such activation may involve the temporary boosting of an electron to a higher orbit or energy state or it may make the molecule vibrate more vigorously thus giving it energy to aid in some subsequent reaction.

We may use a mechanical analogy to assist in understanding activation. Let us imagine a weight resting on a shelf provided with a rim, as in Fig. 1. It will be possible to let the weight do work while falling to the floor by attaching it by means of cord and pulley to a dynamo or other means of absorbing energy. If the rim were absent and the

weight standing on a smooth, oiled shelf, very little energy

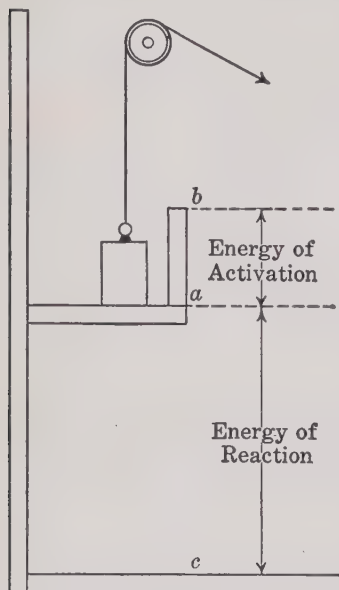


FIG. 1. Illustration of the difference between energy of activation and energy of reaction.

would have to be expended to push the weight over the edge and start the process, but in the arrangement shown, it is necessary to do work on the weight to lift it over the rim in order to start the process. This extra energy is then recovered by reason of the extra height through which the weight falls. We might call the energy required to lift the weight over the shelf, from *a* to *b*, the energy of activation while the energy obtained from *a* to the floor, *c*, is the net energy of the reaction. These two amounts of energy evidently have no necessary connection.

20. Values for the energies of activation are given in Table 1 for several of the reactions considered above.

TABLE 1

REACTION	ENERGY OF ACTIVATION CALS.
$\text{N}_2\text{O}_5 = 2\text{NO}_2 + \text{O}_2$	24,600
$\text{H}_3\text{CN}_2\text{CH}_3 = \text{N}_2 + \text{C}_2\text{H}_6$	52,400
$2\text{HI} = \text{H}_2 + \text{I}_2$	38,900
$\text{H}_2 + \text{I}_2 = 2\text{HI}$	44,000
$2\text{NO}_2 = 2\text{NO} + \text{O}_2$	26,500

21. The magnitude of the heat of activation gives a clue to the temperature at which velocity becomes appreciable, also to the change in velocity with temperature. Thus the first reaction above proceeds with measurable speed at

room temperatures while the second becomes appreciable only around  $300^{\circ}$ .

**22.** The effect of temperature on the velocity constant,  $k$ , is given by the equation:

$$\log \frac{k_2}{k_1} = \frac{E}{4.58} \cdot \frac{T_2 - T_1}{T_1 T_2}$$

where  $k_1$  and  $k_2$  are the values of the velocity constant at  $T_1$  and  $T_2$ , respectively, and  $E$  is the activation. For the decomposition of  $\text{N}_2\text{O}_5$ , for example, we would have, for  $T_2 = 303$  and  $T_1 = 293$ ,

$$\log \frac{k_2}{k_1} = \frac{24,600}{4.58} \cdot \frac{10}{293 \times 303} = 0.605$$

and  $k_2/k_1 = 4$ , *i.e.*, a fourfold increase in velocity for a  $10^{\circ}$  increase in temperature from  $20^{\circ}$  to  $30^{\circ}$  C.

**23.** The rapid increase in reaction velocity with temperature corresponding to the above equation finds a physical explanation in considering the fact that the molecules of a gas have velocities both higher and lower than the mean velocity on which was based the simple discussions in Chapter III. The velocities are distributed among the molecules according to curves shown in Fig. 2,

one curve for a lower temperature,  $T_1$ , the other for a higher temperature,  $T_2$ . Distribution curves of this shape are obtained in a great variety of connections, *e.g.*, the heights or weights of persons; even, indeed, their marks in chemistry, if properly obtained. The curves show that most of the molecules vary but little from the mean of them all, but that there are a few with both very low and very

high velocities. Let us suppose that the velocity  $u$  is required to activate molecules so that they can react in a given case. Evidently the proportion of molecules thus activated increases far more rapidly than the temperature due to the shift of the whole curve to the right for the higher temperature.

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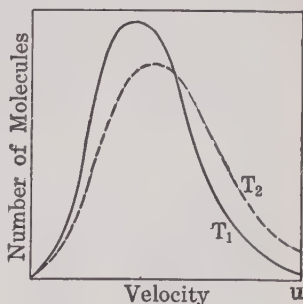


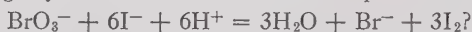
FIG. 2. Distribution of molecular velocity; illustrating the rapid increase with rising temperature of molecules of high velocity.

**24. Explosions.** The heat liberated by a reaction may be dissipated so rapidly that the temperature does not rise appreciably. However, if the heat liberated leaks away

more slowly than it is liberated the temperature of the mass rises, the reaction is accelerated and may finally become quite vigorous. This occurs in spontaneous combustion, say, of oily rags, where oxygen can diffuse into the pile but the heat leaks out only slowly. The combustion becomes more and more rapid until it is limited only by the rate of air access. If the oxygen is already present in some other form, as in gunpowder or dynamite, the reaction, once started, may proceed with explosive velocity. For an explosive to be "safe," there should be high energy of activation, so that it is hard to start. The safest explosives require higher energies than can be given by ordinary mechanical blows, responding only to "detonators" such as "mercury fulminate." The power of an explosive depends on a high energy of reaction. A shattering effect results, as with "T. N. T." (cf. Chapter XVIII, paragraph 24) from high velocity of the explosive wave. A lower velocity is necessary for a propellant powder to correspond with the more gradual acceleration of the projectile.

### EXERCISES

1. Define catalyst.
2. Divide the catalysts mentioned in the text into surface catalysts and dissolved catalysts.
3. What effect may the use of a double boiler have on the speed of cooking food?
4. What means could you employ for rapidly washing photographic prints free from the "hypo" of the fixing bath?
5. How might you alter the time required for developing a photographic negative?
6. How might you endeavor to increase the speed of the reaction:



What effect would acetic acid have upon the speed as compared with hydrochloric acid of the same concentration?

7. The organism existing in "mother of vinegar" converts alcohol into acetic acid by the reaction



By what means could the manufacture of vinegar be hastened?

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## Chapter XII

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### *Chemical Equilibrium. The Effect of Concentration*

**1. Reversibility of Chemical Reactions.** The problem of the control of chemical reactions involves not only the speed, as discussed in Chapter XI, but also the fact that most reactions are reversible. We have, therefore, two problems as distinct from each other as are the speed and destination of a train. To reach a desired destination quickly it is not sufficient to get on a fast train; the train must also go in the right direction. With chemical reactions, similarly, the conditions accelerating the reaction often alter the direction at the same time. For example, the velocity of formation of  $\text{SO}_3$  from  $\text{SO}_2$  and  $\text{O}_2$  increases with the temperature, but the velocity of decomposition of  $\text{SO}_3$  back into  $\text{SO}_2$  and  $\text{O}_2$  is likewise increased thereby, and more rapidly than the velocity of its formation, so that  $\text{SO}_3$  becomes increasingly unstable at higher temperatures. Therefore, assuming that all the time necessary for them to take place is allowed, we will turn our attention to the problem of the direction of chemical reactions. Finally, in Chapter XIV, we will consider both effects together.

**2.** Most chemical reactions are reversible, that is, the products of a reaction may usually be made to react with each other by suitable choice of conditions to produce the original substances. Many examples of this may be given. A liquid may be made to evaporate by raising the temperature or by reducing the pressure, and its vapor, conversely,

may be recondensed to liquid by lowering the temperature or increasing the pressure. Solids may be liquefied by increasing the temperature, and liquids may be solidified by lowering the temperature. Gases may either be dissolved in liquids or driven out of solution by suitable changes in pressure or temperature. The naturally occurring mineral, gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , may be deprived of part of its water by moderate heating, giving plaster of Paris, which is approximately  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ . When this is mixed with water the original dihydrate is re-formed, which causes the plaster to "set," due to the interlocking of the growing crystals of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Nitric oxide,  $\text{NO}$ , is decomposed by gentle heating into nitrogen and oxygen, and yet, at the high temperature of the electric arc a considerable amount of nitric oxide may be formed from the nitrogen and oxygen of air. Oxygen,  $\text{O}_2$ , is changed into ozone,  $\text{O}_3$ , by the silent electric discharge, and then gradually reverts to oxygen again. When a lead storage battery is discharged, the lead dioxide of the positive plate, the lead of the negative plate and the sulfuric acid in the solution react as follows:



and when the battery is recharged the reverse reaction takes place, corresponding to the equation as read from right to left. When water charged with carbon dioxide passes over limestone rock, the following reaction occurs:



The calcium ion dissolved in the water produces what is called "hard water," and interferes with the cleansing power of soap by precipitating insoluble calcium soap. When this water is boiled, however, the  $\text{CO}_2$  is driven off, and the calcium carbonate is re-precipitated, corresponding to the equation as read from right to left. When steam is passed through a tube containing iron filings or nails heated to dull redness, the following reaction occurs:





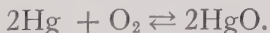
When an excess of hydrogen is passed over the iron oxide,  $\text{Fe}_3\text{O}_4$ , under similar conditions, some of it is changed to steam with the reduction of the oxide to iron, exactly the reverse of the above. Illustrations of reversibility might be multiplied *ad libitum*.

**3. The experimental proof of reversibility** consists simply in mixing each set of substances, as indicated by the two sides of the equation, and seeking conditions under which the other set will be formed. The disappearance of any of the substances taken, or the appearance of any of the products, is usually sufficient proof that a reaction has taken place. What particular substance to test for is determined by the ease and decisiveness of the available tests. Thus the oxidation of mercury, represented by the equation



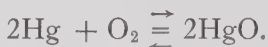
could be proved if conditions could be found under which mercury in contact with oxygen would increase in weight. A change in appearance corresponding to the red color of the oxide, or a decrease in the amount of the gaseous oxygen would suffice equally well. The reverse reaction, the dissociation of mercuric oxide into mercury and oxygen, could be proved by taking the red mercuric oxide and discovering conditions of pressure and temperature under which there could be detected either the appearance of mercury or oxygen, or else a loss in weight.

**4.** It is frequently desirable to express in the equation for a reaction the fact that the reaction is reversible. This is done by substituting a double arrow,  $\rightleftharpoons$ , for the equality sign. Written in this way, an equation such as the last above would appear as follows:



It must be remembered that the double arrow sign retains the full significance of the usual equality sign, merely

adding further information, so that we would do well to regard it as an abbreviation for a fuller representation such as the following:



Since nearly all reactions are reversible, however, the double arrow sign is in reality somewhat superfluous, except, perhaps, where it is desired to emphasize the fact of reversibility. Its absence must never be construed as indicating irreversibility. In view of these facts we will not ordinarily use it in the following pages.

**5. It Is Possible to Have All of the Substances Involved in Reversible Reactions Present Together in Chemical Equilibrium with Each Other.** Instead of passing steam over heated iron in a tube, as in the experiment described above, we might simply heat them together in a closed vessel. We would expect, as before, the formation of some hydrogen and iron oxide, corresponding to the equation as read from left to right. Likewise, if we heat hydrogen and iron oxide together at the same temperature and in a similar vessel, we would expect the formation of iron and steam, corresponding to the equation as read from right to left. If we allow sufficient time for reaction in both cases, how will the final state of affairs in one vessel compare with that in the other? It is obviously absurd to expect either reaction to go to completion, just as it would be absurd to expect a ball placed on a certain table to roll all the way from *a* to *b* when we have previously found that, when placed at *b*, it rolls towards *a*. Obviously there must be some intermediate position on the table at which it tends to come to rest no matter at which end it is started. Again, if it is found that one body becomes cooler when brought into a certain room, and another becomes warmer when brought into the same room, it is evident that each body will come eventually to the same temperature, that of the room, which must lie somewhere between the initial temperatures of the two bodies.

6. By the same kind of reasoning, it should make no difference whether we start with  $3\text{Fe} + 4\text{H}_2\text{O}$ , or with  $\text{Fe}_3\text{O}_4 + 4\text{H}_2$ , if we heat them to a temperature at which they are able to react, in identical vessels, we will eventually get a mixture of all four substances in **chemical equilibrium**. The term chemical equilibrium signifies an adjustment of the amounts of the reacting substances such that there is no further tendency to react, just as in mechanical equilibrium we have an adjustment of forces such that no further action takes place. This adjustment of the amounts of substances in chemical equilibrium may be thought of as the result of an adjustment between chemical forces. Just as a balance loaded with certain weights will finally come to rest, provided that the balance is free to swing, at a position dependent only upon the weights on the pans and not upon the direction in which an original displacement took place, so in a reversible chemical reaction, the final equilibrium between the amounts of the reacting substances, provided that they are free to react (suitable temperature, catalyst, etc.), will depend only on the relative amounts of the substances present, and not upon which particular set of substances, as represented by the two sides of the equation, is chosen. There is, of course, no oscillation in reaching chemical equilibrium comparable to that of a balance in coming to rest.

7. From a kinetic standpoint, chemical equilibrium must be regarded as the result of two opposite reactions proceeding with equal speed. When, for example, we start with iron and steam, at a sufficiently high temperature, they react with a velocity depending on the concentration of steam molecules and on the surface of the iron. As these are used up the reaction gradually becomes slower. At the same time, as more hydrogen and iron oxide are produced, they begin to react with each other to regenerate the iron and steam, with an increasing velocity, until the rate of one reaction just equals that of the other. This conception

of equilibrium was used in connection with simpler phenomena in Chapter III, and has an important bearing on what is here to follow.

**8. The Effect on Chemical Equilibrium of Changing the Concentration of the Reacting Substances.** If a little weight is added to or taken from one pan of a balance in equilibrium, the pointer swings a little to one side or the other until a new position of equilibrium is reached. Similarly, when a chemical equilibrium exists, it is possible to disturb it by any means which changes the relative speeds of the two opposing reactions. These rates may be affected by changing the temperature, or the total pressure on the reacting system, or the concentration of the substances involved. The effect of changing the temperature or total pressure will be discussed in Chapter XIV, and we will turn our attention first to changes in concentration.

9. If we recall the kinetic conception of chemical equilibrium, we will see that if we increase the concentration of one of the reacting substances, there are then more molecules of that substance present in a given space, so that their ability to find and react with other molecules is increased. This will cause a temporary gain in the rate of the reaction using up this kind of molecule, until more of the products of this reaction, represented on the other side of the equation, are produced, so as to equalize again the rates of the two reactions. The net result is that the reaction proceeds to some extent in the direction which will use up the substance whose concentration is thus increased.

10. For illustration let us consider a closed vessel containing  $\text{SO}_3$ ,  $\text{SO}_2$  and  $\text{O}_2$  in chemical equilibrium, to attain which requires a sufficiently high temperature and perhaps a catalyst. When equilibrium is attained we must imagine that the two reactions, represented by the equation



read in both directions, are taking place with equal veloc-

ities, with a net result of no change in the relative amounts of the three gases present. Suppose, now, that more oxygen is introduced into the vessel. The increased number of oxygen molecules will render it easier for them to collide with sulfur dioxide molecules, resulting in a more rapid formation of sulfur trioxide molecules. As the number of the latter increase their own speed of decomposition will increase until the two reactions again take place at equal rates. The net effect of this increase in the amount of oxygen is to cause more of it to be used up, with a decrease in the amount of sulfur dioxide and an increase in the amount of sulfur trioxide. The effect of adding or removing any of the three substances present can be predicted on the above basis.

From a technical point of view, in making sulfur trioxide, the important thing is to use up the sulfur dioxide as completely as possible, since the latter costs money, whereas the supply of oxygen is free. To accomplish this the kinetic theory indicates that it is desirable to have the oxygen in excess, since otherwise considerable sulfur dioxide would remain uncombined when equilibrium has been reached.

**11.** In general, after equilibrium has been reached, **the effect of any change in the concentration of the reacting substances is to cause that reaction to take place which tends to neutralize the change**; that is, if the concentration of any substance is increased, that reaction tends to take place which uses up that substance, and where the concentration of any substance is decreased, that reaction tends to take place which will replace that substance. This conclusion is a special case of a more general one, called the **Theorem of Le Chatelier**, which states that when equilibrium has been reached a change in *any* of the factors affecting equilibrium tends to make that reaction take place which will neutralize the effect of the change. The discussion of other factors will be taken up in Chapter XIV.

**12.** The above conclusion, in so far as concentration alone



is concerned, is called the "Law of Mass Action," or the "Mass Law." This name is slightly misleading, since it is not the masses of the substances present, but their concentrations, or masses per unit volume, which determine equilibrium. This point was discussed in Chapter III, where it was shown that the depth of the water in equilibrium with its vapor, or the extent of the surface between the two phases, has no effect upon the equilibrium. On the other hand, a change in the concentration of the vapor, as by changing its volume, or in the concentration of the liquid, as by adding some other substance to it, *would* cause some reaction to take place. Likewise, in the equilibrium discussed above, between iron, its oxide, steam and hydrogen, the relative amounts of the solids have no more effect than would the addition of more salt to a saturated salt solution. The reaction takes place where the three phases, the two solids and the gas phase, are in contact, and its rate does not depend on the excess of either solid.

**13.** These same conclusions apply to reactions occurring in solution, including those between ionized substances. For example, that the reaction



will take place as read from left to right may be shown by taking pure acetic acid (which is un-ionized, as shown by its being a non-conductor) and dissolving it in water, when the solution will have the properties of hydrogen ion. That the reaction will also take place as read from right to left, may be shown by mixing a solution of a strong acid, like hydrochloric acid, giving a large concentration of hydrogen ion, with one of sodium acetate, which gives a large concentration of acetate ion. We find that hydrogen ion disappears partly from the solution, and also that acetic acid appears, as is evident by its odor. It makes no difference, therefore, whether we start with a mole of acetic acid in a liter of water, or with a mole each of hydrogen and acetate



ions in a liter of water, the final state of affairs is the same, which is that we will have present about 0.004 mole of each of the two ions and 0.996 mole of the undissociated molecules. If, subsequently, we add another mole of acetate ion (in solution with, say, sodium ion, which affects none of the substances present) some of the acetate ion will be able to use up more of the hydrogen ion, becoming acetic acid, resulting in a considerable decrease in the acidity (hydrogen ion concentration) of the solution.

**14.** The dilution of a solution of a weak electrolyte such as acetic acid results in an increase in the degree of dissociation (cf. page 113), as can readily be deduced by the aid of the kinetic picture of equilibrium. At equilibrium there are just as many molecules of acetic acid splitting into ions as are being reformed from the ions in a given time. If more water is added the rate of the ionization process can be little affected, since the acetic acid molecules in both solutions are surrounded entirely by water molecules. However, the  $\text{H}^+$  and  $\text{C}_2\text{H}_3\text{O}_2^-$  are farther apart, on the average, after the dilution, and cannot collide and reunite so frequently, so that the former reaction gains upon the latter, and the resulting increase in the number of ions increases the frequency of collision till the rate of recombination again equals the rate of dissociation. The net result of the dilution is, therefore, that more of the acid has ionized as expressed by the equation:  $\text{HC}_2\text{H}_3\text{O}_2 = \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^-$ .

**15.** These conclusions are so important, and of such general validity, applying to gaseous as well as ionic equilibria, that we will emphasize them by the tabulation of the acetic acid equilibrium given in Table 1. The figures have been calculated by a method to be outlined later. Their relative, rather than their absolute, magnitudes should here receive attention. A comparison of cases A and B shows that the amounts of each of the three substances present at equilibrium are identical, regardless of the direction from

which it has been reached. Case C shows the large diminution of  $H^+$ , and the consequent increase in  $HC_2H_3O_2$ , following an increase in the amount of  $C_2H_3O_2^-$ . Case D shows the corresponding diminution of  $C_2H_3O_2^-$ , following the addition of an excess of  $H^+$ . Case E shows the increase in the degree of dissociation caused by dilution. Chemists are accustomed to refer to the change from one condition

TABLE 1

	$HC_2H_3O_2 = H^+ + C_2H_3O_2^-$			VOLUME OF SOLUTION, LITERS	DIRECTION AND MOLES OF ACID IONIZED OR FORMED
A Take, moles	1	0	0	1	
Get, at equilibrium,	0.996	0.004	0.004	1	0.004 →
B Take, by mixing $H^+ + Cl^-$ with $Na^+ + C_2H_3O_2^-$ ,	0	1	1	1	
Get, at equilibrium,	0.996	0.004	0.004	1	0.996 ←
C Take above equilib. mixture,	0.996	0.004	0.004	1	
Add 0.1 mole each $Na^+ + C_2H_3O_2^-$ , get	1.00	0.0002	0.10	1	0.004 ←
D Take equilib. mixture,	0.996	0.004	0.004	1	
Add 0.1 mole each $H^+ + Cl^-$ , get	1.00	0.10	0.0002	1	0.004 ←
E Take equilib. mixture,	0.996	0.004	0.004	1	
Dilute to 10 l., get	0.987	0.013	0.013	10	
Conc.	0.0987	0.0013	0.0013	1	0.009 →

of equilibrium to another, such as cases C, D and E, as a **shift of equilibrium** to the left (Cases C and D) or to the right (E) as the case may be.

It is to be noted that the equation, read either to the right or the left, does not in itself tell how much material has reacted or what are the equilibrium concentrations, but only that if acetic acid is allowed to ionize, due to putting it into water, or by increasing the ionization by adding more water to a mixture in equilibrium, every molecule of acetic acid that ionizes forms one hydrogen ion and one acetate ion; again, if acetic acid molecules are formed, as by evaporation, or the processes stated in B, C and D, the ions unite in the proportion one to one. In case C a large excess of  $\text{C}_2\text{H}_3\text{O}_2^-$  had to be added to use up 0.0038 mole of  $\text{H}^+$ , but only 0.0038 mole of  $\text{C}_2\text{H}_3\text{O}_2^-$  out of the 0.1 mole added combined with  $\text{H}^+$ . The presence of five hunters instead of one hunting for a rabbit in a certain tract of land greatly shortens the life expectation of the rabbit, but only one of the hunters bags the rabbit.

**16. Quantitative Expression of the Mass Law.** In the above discussion of the effect of concentration on chemical equilibrium we have been content with predicting the direction of the effect of altering concentration, the qualitative effect, without inquiring how much a given equilibrium would be disturbed by a certain change in concentration of one or more of the reacting substances. This would be called the quantitative effect. Although the qualitative prediction suffices in most cases, it is nevertheless often desirable to make a quantitative prediction. This is possible by combining the quantitative expression for the speed of a chemical reaction, given in Chapter XI, with the idea introduced in this chapter, that at equilibrium the two opposite reactions are proceeding with equal velocity. For the sulfur trioxide reaction discussed above, we would have for the velocity of formation  $v_1 = k_1 c_{\text{SO}_2}^2 \cdot c_{\text{O}_2}$ , where  $k_1$  is a constant. Similarly, for the decomposition of the trioxide

back into the dioxide and oxygen, we would have for the velocity  $v_2 = k_2 c_{\text{SO}_3}^2$ . At equilibrium the two velocities are equal, so that  $k_1 c_{\text{SO}_2}^2 \cdot c_{\text{O}_2} = k_2 c_{\text{SO}_3}^2$ . Since  $k_1$  and  $k_2$  are constants their quotient is a constant,  $K$ , so that we may write

$$\frac{c_{\text{SO}_3}^2}{c_{\text{SO}_2}^2 c_{\text{O}_2}} = K.$$

17. By means of this expression we are able to make qualitative as well as quantitative predictions. Since  $K$  is constant at a given temperature, the values of the three concentrations must always adjust themselves accordingly. For example, suppose that it were found by measurement, at a certain temperature, that when equilibrium was reached the concentrations were as follows:  $\text{SO}_2$ , 3 moles per liter,  $\text{O}_2$ , 1 mole per liter,  $\text{SO}_3$ , 2 moles per liter. By substituting these values in the above expression we obtain for the value of the constant  $K = \frac{4}{9}$ . From this we can calculate another set of equilibrium concentrations. Thus, if the concentration of  $\text{O}_2$  were 5 moles per liter, and that of  $\text{SO}_3$  2 moles per liter, we would have

$$\frac{4}{c_{\text{SO}_2}^2 \times 5} = \frac{4}{9}$$

from which we would find the concentration of  $\text{SO}_2$  in equilibrium with sulfur trioxide and oxygen at the new concentrations to be 1.34 moles per liter.

18. It is also the custom to denote concentrations by the formula of the substance inclosed in brackets or parentheses. Using this notation we would write the above expression

$$\frac{(\text{SO}_3)^2}{(\text{SO}_2)^2 (\text{O}_2)} = K,$$

which has exactly the same significance as before when  $c$  was used to denote concentration.

19. In the derivation of the equilibrium equation from the velocity equations in the manner just given we have ignored the fact, noted in the preceding chapter, that many reactions proceed in steps, one of which may be slower than the others and hence determines the rate. Such a state of affairs does not, as might be supposed at first sight, vitiate the equilibrium equation based on the total reaction, as can be seen from the following case: the equilibrium constant of the reaction  $3\text{HNO}_2 =$

$$2\text{NO} + \text{H}_2\text{O} + \text{H}^+ + \text{NO}_3^- \text{ is } K = \frac{(\text{NO})^2(\text{H}^+)(\text{NO}_3^-)}{(\text{HNO}_2)^3}. \quad (\text{The concen-}$$

tration of the water remains practically constant in dilute solutions.) The velocity equations, however, are not  $v_1 = k_1(\text{HNO}_2)^3$  and  $v_2 = k_2(\text{NO})^2(\text{H}^+)(\text{NO}_3^-)$ , for the reaction actually takes place in two stages,  $4\text{HNO}_2 = \text{N}_2\text{O}_4 + 2\text{NO} + 2\text{H}_2\text{O}$ , which is rapid and reversible, and  $\text{N}_2\text{O}_4 + \text{H}_2\text{O} = \text{HNO}_2 + \text{H}^+ + \text{NO}_3^-$ , which is slow, and determines the rate. There are, therefore, two rates from left to right,  $v_1 = k_1(\text{HNO}_2)^4$  and  $v'_1 = k'_1(\text{N}_2\text{O}_4)$ , also two to the left,  $v_2 = k_2(\text{N}_2\text{O}_4)(\text{NO})^2$  and  $v'_2 = k'_2(\text{HNO}_2)(\text{H}^+)(\text{NO}_3^-)$ . At equilibrium  $v_1 = v_2$  and  $v'_1 = v'_2$ , therefore

$$\frac{k_1}{k_2} = \frac{(\text{N}_2\text{O}_4)(\text{NO})^2}{(\text{HNO}_2)^4} \text{ and } \frac{k'_1}{k'_2} = \frac{(\text{HNO}_2)(\text{H}^+)(\text{NO}_3^-)}{(\text{N}_2\text{O}_4)}$$

from which

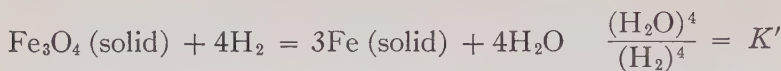
$$\frac{k_1 k'_1}{k_2 k'_2} = \frac{(\text{NO})^2(\text{H}^+)(\text{NO}_3^-)}{(\text{HNO}_2)^3},$$

which is a constant, since the small  $k$ 's are all constants, identical with  $K$ , above.

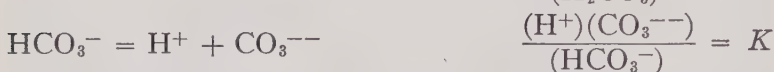
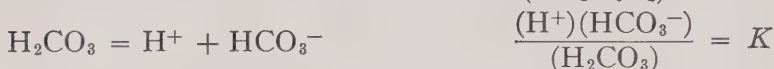
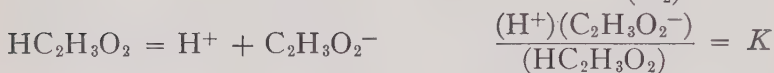
20. It may be worth while to give examples of the equilibrium equation for several other reactions.

REACTION	EQUILIBRIUM EQUATION
$\text{N}_2 + \text{O}_2 = 2\text{NO}$	$\frac{(\text{NO})^2}{(\text{N}_2)(\text{O}_2)} = K$
$\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$	$\frac{(\text{NH}_3)^2}{(\text{N}_2)(\text{H}_2)^3} = K$
$\text{CO}_2 + \text{C (solid)} = 2\text{CO}$	$\frac{(\text{CO})^2}{(\text{CO}_2)} = K$

(Since carbon is solid its concentration is constant and need not be expressed in the equilibrium equation.)



$$\text{or} \quad \frac{(\text{H}_2\text{O})}{(\text{H}_2)} = K$$



21. Since the partial pressure of a gas is proportional to the number of molecules in a given space, and hence to the concentration, it is possible, where gases are concerned, to write partial pressures instead of concentrations, and have constant a similar function of partial pressures. This constant is not necessarily the same as that where concentrations are used, so that we will express it as  $K_p$ . We would write, accordingly,

$$\frac{p_{\text{NO}}^2}{p_{\text{N}_2} \cdot p_{\text{O}_2}} = K_p, \quad \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} \cdot p_{\text{H}_2}^3} = K_p, \text{ etc.}$$

22. **Dissociation Constants of Electrolytes.** The equilibrium constants for the dissociation of an electrolyte, as with acetic and carbonic acids above, are often called **dissociation constants** or **ionization constants**, and express the strength of an acid or base in the most general way. It is evident that the stronger the electrolyte the larger are the concentrations written in the numerator of the fraction, hence the larger the dissociation constant. Instead of stating the degree of dissociation for an electrolyte at a certain concentration, as was done in Chapter VIII, paragraph 13, it is more satisfactory to give the dissociation constant, from which the degree of dissociation at any concentration may be calculated. The following values for certain familiar substances may be given:



TABLE 2

SUBSTANCE	REACTION	DISSOCIATION CONSTANT AT ROOM TEM- PERATURE *
Acetic acid . . . . .	$\text{HC}_2\text{H}_3\text{O}_2 = \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^-$	$1.8 \times 10^{-5}$
Dihydrogen phosphate ion . . . . .	$\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{--}$	$6 \times 10^{-8}$
Carbonic acid . . . . .	$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$	$4.3 \times 10^{-7}$
Hydrogen sulfide . . . . .	$\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$	$10^{-7}$
Hydrocyanic acid . . . . .	$\text{HCN} = \text{H}^+ + \text{CN}^-$	$4 \times 10^{-10}$
Bicarbonate ion . . . . .	$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{--}$	$4.7 \times 10^{-11}$
Hydrosulfide ion . . . . .	$\text{HS}^- = \text{H}^+ + \text{S}^{--}$	$10^{-15}$
Ammonium hydroxide . . . . .	$\text{NH}_4\text{OH} = \text{NH}_4^+ + \text{OH}^-$	$1.8 \times 10^{-5}$
Bisulfate ion . . . . .	$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{--}$	$1.2 \times 10^{-2}$

\* All of these values have to be increased for solutions containing high concentrations of other ions, which aid in dissociating the weak electrolyte.

**23.** The concentration of hydrogen ion in a solution of acetic acid, for example, may be calculated from the dissociation constant of the acid as follows: If the acid alone is present in the solution, the hydrogen ion and the acetate ion are at the same concentration, hence  $(\text{H}^+) = (\text{C}_2\text{H}_3\text{O}_2^-)$ . Suppose that the total concentration of acetic acid is 0.1 molal. The amount ionizing is so slight that the un-ionized acid may be considered as 0.1 molal without appreciable error, *i.e.*,  $(\text{HC}_2\text{H}_3\text{O}_2) = 0.1$ . Substituting these values in the equilibrium equation, we obtain

$$\frac{(\text{H}^+)^2}{0.1} = 1.8 \times 10^{-5} \text{ and hence } (\text{H}^+) = 0.0013.$$

Again, suppose that 0.05 molal acetate ion is present in the same solution, then  $(\text{C}_2\text{H}_3\text{O}_2^-) = 0.05$ ,  $(\text{HC}_2\text{H}_3\text{O}_2) = 0.1$  and  $(\text{H}^+) = 0.000036$ . It will be observed that the acidity of this solution is vastly less than that of the former.

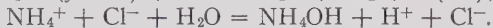
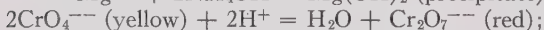
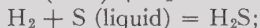
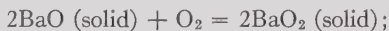
**24.** Strong electrolytes do not obey the Mass Law, for reasons which there is not space here to discuss, so that calculations such as the above cannot be made with them. However, little is lost on this account, as they may be considered, with approximate accuracy, as completely dissociated.

**25. Catalysts Do Not Shift Equilibrium.** On page 139 we considered the catalyst as an agent for altering the speed of a reaction. We must now note that in the case of reactions which come to equilibrium the catalyst for the reaction in one direction must also be a catalyst for the reverse reaction, and that the catalyst can have no effect upon equilibrium, but only upon the speed with which it is attained. If a catalyst could shift equilibrium, we could use a gas reaction involving a change in the number of molecules, and by alternately putting in and taking out the catalyst, which would require little effort, we could produce an alternate increase and decrease in pressure which could do useful work at no expense, which is contrary to the evident morality of nature.

It is true that by the use of a catalyst we may reach equilibrium in a so much shorter time that we may be able to work at a lower temperature, where equilibrium is more favorable, but it is then the temperature not the catalyst which has shifted the equilibrium.

### EXERCISES

1. Describe experiments which would prove whether or not the following reactions can be made to take place in both directions:



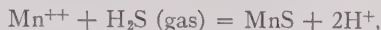
2. Hard water may be softened by means of an insoluble substance called zeolite,  $\text{Na}(\text{H}_6\text{AlSiO}_7)$ , which exchanges the calcium (or magnesium) ion in the water for sodium ion as follows:



Can you suggest a way of restoring the sodium zeolite after it has all been changed to calcium or magnesium zeolite?

3. Describe in words the effect of adding solid sodium acetate to a solution of acetic acid, and write an equation for the reaction.

4. The precipitation of manganese ion as manganese sulfide, according to the equation,



is never complete. How would you make the amount precipitated as great as possible? How would you redissolve all of the precipitate?

5. Write equations showing what happens when (a) 2 moles of hydrogen are mixed with 4 moles of oxygen and an electric spark passed; (b) dilute solutions containing respectively 1 mole of hydrochloric acid and 2 moles of sodium acetate are mixed.

6. Using the equilibrium constants given in Table 2, calculate the ( $\text{H}^+$ ) for the first five acids and the ( $\text{OH}^-$ ) for ammonia when the substance is present in 0.05 molal solution.

*Ans.*  $10^{-3}$ ;  $10^{-4}$ ;  $1.3 \times 10^{-4}$ ;  $0.7 \times 10^{-4}$ ;  $0.8 \times 10^{-5}$ ;  $10^{-3}$ .

7.  $\text{N}_2\text{O}_4$  gas under certain conditions is dissociated to give  $2\text{NO}_2$ . On the basis of kinetic theory predict the effect of volume change on this reaction.

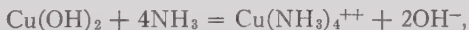
8. 0.1 *N* anthranilic acid ( $\text{HC}_7\text{H}_6\text{NO}_2$ ) is 1% dissociated. (a) What is its  $\text{H}^+$  ion concentration? (b) What volume of 0.2 *N*-NaOH is necessary to neutralize 50 cc. of this solution? (c) When it is neutralized by NaOH what substances are present in the final solution? *Ans.* 0.001 *M*; 25 cc.

9. Explain by the kinetic theory how the equilibrium  $\text{H}^+ + \text{C}_6\text{H}_5\text{COO}^- = \text{C}_6\text{H}_5\text{COOH}$  should be shifted by dilution with water.

10. State in words what happens when a solution of NaAc is added to a saturated solution of AgAc.

11. Of the following factors, which influence the solubility and which the rate of solution of a salt: (a) size of particles; (b) temperature; (c) stirring; (d) excess of salt?

12. If the substances represented in the following equation are all present in equilibrium with each other,



what will be the effect upon the amount of  $\text{Cu(OH)}_2$  present if (1) the mixture is boiled, (2) if NaOH is added, (3) if  $\text{K}_2\text{SO}_4$  is added, (4) if  $(\text{NH}_4)_2\text{SO}_4$  is added?

13. If  $\text{H}^+$ ,  $\text{Ac}^-$  and  $\text{HAc}$  are present in a solution in equilibrium, explain, in terms of the kinetic theory, what will happen if you add (a) water, (b) NaAc solution, (c) HCl solution.

14. If  $\text{NH}_4^+$ ,  $\text{OH}^-$ ,  $\text{NH}_4\text{OH}$  and  $\text{NH}_3$  are present in water in equilibrium with each other, explain in terms of the kinetic theory what will happen if you add (1) water, (2)  $\text{NH}_4\text{Cl}$ , (3) NaOH, (4) NaCl, (5)  $\text{NH}_3$  gas.

15. State two ways of shifting the equilibrium  $2\text{HCO}_3^- = \text{H}_2\text{CO}_3 + \text{CO}_3^{--}$  so as to decrease the amount of  $\text{HCO}_3^-$ .

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## Chapter XIII

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### *Types of Equilibria*

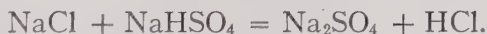
1. We have seen, in Chapter XII, that it is possible to control reactions which come to equilibrium by changing the concentrations of the reacting substances. A reaction may be made more complete by using the reacting substances at greater concentration, or by removing one or more of the products of the reaction. We may now ask the questions: In what ways may substances be added to or taken away from reacting mixtures, and what properties of substances determine whether a reaction proceeds more completely in one direction or another? The ability to answer these questions enables one, without previous experiment, to predict and control reactions in a large number of cases. It is important that the amount of experimental material to be memorized should be the minimum necessary to deal with the vast number of reactions likely to be encountered. How this material may be arranged and applied will be shown in the following pages.

2. **Volatility.** One of the properties of substances that may be utilized in bringing about reactions is volatility. If a certain reacting mixture is in an inclosed space, equilibrium may be reached long before all of the desired products are obtained; but if one of the substances produced is volatile at the temperature of the reaction, it may be allowed to escape, or be pumped off, and its removal will allow more of it to be formed, according to the principle set forth in the last chapter. If this removal is continued, it

may be possible to make the reaction go to completion. For example, if solutions of sodium chloride and sulfuric acid are mixed, there is only a small tendency to form hydrochloric acid, since the latter is a little stronger than the former. However, since hydrogen chloride, in the absence of water, is a gas, it is possible to produce it by the reaction between *solid* sodium chloride and *concentrated* sulfuric acid, as follows:



If this were done in a closed vessel, equilibrium would be reached before much of the salt and sulfuric acid had reacted in this way; but if the vessel is open, so that the HCl gas can escape, then it can all be removed, and the reaction may go to completion. Further heating, if enough salt is present, will give neutral sodium sulfate,  $\text{Na}_2\text{SO}_4$ , the second step being



The more volatile acid is thus driven out of its salt by the less volatile one. This principle is used in the manufacture of hydrochloric acid, where the gas is caught and dissolved in water. A number of other acids are obtained commercially from their salts by heating them with sulfuric acid in the same way, among them nitric acid,  $\text{HNO}_3$ , from the naturally occurring  $\text{NaNO}_3$ ; hydrofluoric acid,  $\text{HF}$ , from fluorspar,  $\text{CaF}_2$ ; acetic acid from calcium acetate,<sup>1</sup> etc.

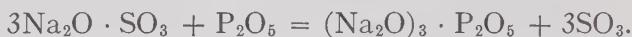
3. Sodium sulfate, on the other hand, may be changed to sodium phosphate by using  $\text{P}_2\text{O}_5$ , which is less volatile than  $\text{SO}_3$ . The reaction is



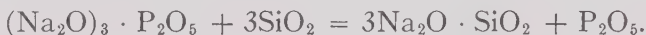
This is a case where it may be more satisfactory to consider

<sup>1</sup>When wood is distilled the acetic acid is separated from the wood alcohol, acetone, etc., occurring in the distillate, by using slaked lime,  $\text{Ca}(\text{OH})_2$ , in order to convert it into the non-volatile calcium acetate.

the salts as combinations of the metallic and non-metallic oxides, as explained in Chapter V. The equation is



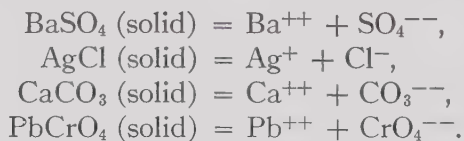
Again, since  $\text{SiO}_2$  is still less volatile than  $\text{P}_2\text{O}_5$ , a phosphate may be changed to a silicate by heating it to a sufficiently high temperature with  $\text{SiO}_2$ , as follows:



In solution, where the difference in volatility of the above substances would not be evident, the reverse changes only would take place, since silicic, phosphoric and sulfuric acids are successively stronger, as will be explained presently.

It is well to remember that ammonium salts are easily volatilized, and that many chlorides are rather volatile, especially  $\text{HgCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{SbCl}_3$ ,  $\text{SbCl}_5$ ,  $\text{AsCl}_3$ ,  $\text{SnCl}_4$ .

**4. Solubility.** The solubilities of substances have an important bearing on the course of reactions. When a rather insoluble salt is put into water a little of it dissolves, for almost no salts are so insoluble that the amount going into solution cannot be measured. The small quantity which does dissolve will be ionized, since nearly all salts are ionized in so far as they will go into solution. The equation expressing the reaction when such a salt is put into water should express this ionization, as exemplified by the following:



When the solution is saturated there will be equilibrium between the solid salt, represented on the left side of each equation, and its ions in solution, represented on the right. The observed fact that all the above salts are only very slightly soluble means that the solutions will contain but



very little of their ions. It also enables us to predict that if we mix the ions of any of the salts at any considerable concentration, they will react almost completely to form a **precipitate** (from a Latin word meaning to throw down) of the corresponding salt. A knowledge of the solubilities of salts, therefore, enables us to tell what ions will precipitate each other from solution. No matter what other ions are present, no matter from what compounds they are obtained,  $\text{Ba}^{++}$  and  $\text{SO}_4^{--}$  in any appreciable concentration will always form a precipitate of  $\text{BaSO}_4$ . Moreover, if it is desired to remove  $\text{Ba}^{++}$  from solution most completely, our knowledge of equilibrium indicates that we should add an excess of  $\text{SO}_4^{--}$ . This effect is constantly sought in quantitative analysis.

5. Conversely, if we wish to dissolve a precipitate, we must endeavor to remove from the solution one of its ions. This removal, in the case of ions, is not so simple as is the removal of a gas, but requires a knowledge of other combinations the ion is capable of forming, as we will see later.

6. Which of the two salts of a common ion will be precipitated depends on their relative solubility and the relative concentrations of the ions in question. If to a mixture of chloride and iodide ions is added a solution of silver ion, silver iodide, yellow, is formed before silver chloride, white. This shows that  $\text{AgI}$  is less soluble than  $\text{AgCl}$ , or, in other words,  $\text{I}^-$  removes  $\text{Ag}^+$  from solution more completely than does  $\text{Cl}^-$  at the same concentration. This would also enable us to predict that if we start with  $\text{AgCl}$  we might bring about the following transformation quite readily:



whereas the reverse reaction could only be brought about by keeping the concentration of  $\text{I}^-$  very small and that of  $\text{Cl}^-$  very large, as would be the case in continual washing of the  $\text{AgI}$  precipitate on a filter with a solution of  $\text{Cl}^-$ . If, subsequently, we find that  $\text{Ag}_2\text{CO}_3$ , silver carbonate, is

readily transposed into  $\text{AgCl}$  by allowing  $\text{Cl}^-$  to act upon it, then we know that  $\text{Ag}_2\text{CO}_3$  is more soluble than either of the others, or, in other words, carbonate ion,  $\text{CO}_3^{--}$ , removes  $\text{Ag}^+$  from solution less completely than either  $\text{Cl}^-$  or  $\text{I}^-$ , and without trying it, we could predict with assurance that the following reaction would take place very readily as read from left to right, but not in the reverse direction:



Again, on finding by experiment that  $\text{AgI}$  is readily changed into  $\text{Ag}_2\text{S}$  by  $\text{SH}^-$ , we could conclude that both of the other precipitates could be transposed into  $\text{Ag}_2\text{S}$  still more easily. It will be seen that with the aid of the ideas of equilibrium we are able to predict a large number of reactions on the basis of a few well-chosen experiments, and thus utilize our experimental knowledge to the best advantage.

7. The same considerations apply to relatively insoluble acids and bases. Magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ , when put into water, dissolves slightly, forming its ions as follows:



Therefore if solutions of, say, magnesium chloride and sodium hydroxide are mixed, a precipitate of  $\text{Mg}(\text{OH})_2$  will be formed.

8. Since knowledge of the solubilities of salts, acids and bases in water is evidently extremely important in enabling one to predict and control reactions, some useful generalizations are given below.

As far as the relation between solubility and other properties is concerned, we may note that, other things being equal, **the higher the melting point of the compound the less soluble it will be**, not only in water, but in any solvent. Also, where the melting points are approximately the same, **the compounds most soluble in water will be those in which**

there is the greatest difference in the positive and negative character of the constituent parts (see Chapter V), so that the salts of a metal like silver will be less soluble than those of a metal like potassium. These rough conclusions are illustrated by the values in Table 1.

TABLE 1

SUBSTANCE	MELTING POINT	SOLUBILITY AT 20°, IN MOLES PER 1000 GRAMS OF SOLUTION
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . . . . .	30°	1.9
$\text{H}_3\text{BO}_3$ . . . . .	185°	0.077
$\text{AgNO}_3$ . . . . .	218°	4.3
$\text{NaNO}_3$ . . . . .	333°	5.5
$\text{AgCl}$ . . . . .	455°	0.00001
$\text{KCl}$ . . . . .	722°	3.3
$\text{BaCO}_3$ . . . . .	795°	0.0001
$\text{PbSO}_4$ . . . . .	1100°	0.00015
$\text{CaF}_2$ . . . . .	1400°	0.0002
$\text{CaSiO}_3$ . . . . .	1510°	0+
$\text{BaSO}_4$ . . . . .	1580°	0.00001

9. A number of statements may be made regarding the compounds of particular ions such as the following. It must be understood, however, that only the commoner compounds are considered:

All nitrates are soluble.

All acetates are soluble ( $\text{AgC}_2\text{H}_3\text{O}_2$  only moderately).

All chlorides are soluble, except  $\text{AgCl}$ ,  $\text{HgCl}$ ,  $\text{PbCl}_2$  (the last is sparingly soluble in cold water, moderately soluble in hot).

All sulfates are soluble, except  $\text{BaSO}_4$ ,  $\text{PbSO}_4$  ( $\text{CaSO}_4$ ,  $\text{Hg}_2\text{SO}_4$  and  $\text{Ag}_2\text{SO}_4$  are sparingly soluble).

All carbonates and phosphates are insoluble, except those of sodium, potassium and ammonium. (Many acid phosphates are soluble, *e.g.*,  $\text{Mg}(\text{H}_2\text{PO}_4)_2$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and  $\text{Ba}(\text{H}_2\text{PO}_4)_2$ .)

All hydroxides are insoluble, except  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{NH}_4\text{OH}$  and  $\text{Ba}(\text{OH})_2$ ;  $\text{Ca}(\text{OH})_2$  is sparingly soluble.

All sulfides are insoluble, except those of sodium, potassium and ammonium. Those of magnesium, calcium, barium and aluminum are not precipitated from solution because they are decomposed by water.

All salts of sodium, ammonium and potassium are soluble, except  $\text{Na}_4\text{Sb}_2\text{O}_7$ ,  $(\text{K or NH}_4)_2\text{PtCl}_6$  and  $(\text{K or NH}_4)_3\text{Co}(\text{NO}_2)_6$ .

All silver salts are insoluble, except  $\text{AgNO}_3$ ,  $\text{AgC}_2\text{H}_3\text{O}_2$ ,  $\text{Ag}_2\text{SO}_4$  (the last two are moderately soluble).

**10.** It is upon the basis of solubilities that different ions present in the same solution may be separated. Suppose, for example, that a solution contained the nitrates of silver, barium, zinc and potassium. The addition of chloride ion, using, say, a solution of ammonium chloride, would precipitate the silver ion as  $\text{AgCl}$ , which could be filtered out. The addition, then, of sulfate ion, as by using ammonium sulfate solution, would precipitate the barium ion as  $\text{BaSO}_4$ . After this is filtered out, the zinc ion could be precipitated as sulfide, using ammonium sulfide. The excess of ammonium salts in the solution could finally be removed by evaporating the solution to dryness and heating the residue, which would volatilize the ammonium salts, leaving only the potassium salts.

**11. Ionization of Water.** It was shown in Chapter VIII that water is an extremely weak electrolyte, dissociating to a minute extent as follows:



In pure water we have  $(\text{H}^+) = (\text{OH}^-) = 10^{-7}$  moles per liter. This is very slight indeed, but we shall see that it is very important. If an excess of either of the ions  $\text{H}^+$  or  $\text{OH}^-$  is added to water, as in dissolving an acid or base in it, the result is a diminution in the concentration of the other. If, for example,  $0.001\text{ }M\text{-HCl}$  is present, the concentration of the hydrogen ion is increased 10,000 times, which will cause that of the hydroxide ion to decrease 10,000 times,

becoming  $10^{-11}$ . This inverse relationship is shown in the first two columns of Table 2.

12. We may conclude, from the slightness of this ionization, that the reverse reaction will take place almost completely, so that whenever an acid and a base are mixed they will react almost completely to form water, leaving the other ions in solution, unless they happen to form an insoluble substance. We must therefore regard neutralization of acids and bases as taking place because of the fact that water is almost entirely undissociated. In connection with the neutralization of weak acids and bases we will return later to this topic.

TABLE 2  
APPROXIMATE INDICATOR COLORS

CONC. OF $H^+$	CONC. OF $OH^-$	pH *	METHYL VIOLET	METHYL ORANGE	BROMPHENOL BLUE	BROMCRESOL GREEN	LITMUS	BROMTHYMOL BLUE	THYMOL BLUE	PHENOLPHTHALEIN	ALIZARIN YELLOW R	INDIGO CARMINE	SOLUTIONS OF CERTAIN COMMON SUBSTANCES
1	$10^{-14}$	0	v	r	y	y	r	y	r	c	y	b	1 M-HCl
$10^{-1}$	$10^{-13}$	1	s	r	y	y	r	y	o	c	y	b	0.1 M-HCl
$10^{-2}$	$10^{-12}$	2	b	r	y	y	r	y	y	c	y	b	
$10^{-3}$	$10^{-11}$	3	v	r	y	y	r	y	y	c	y	b	0.05 M- $HC_2H_3O_2$
$10^{-4}$	$10^{-10}$	4	v	o	g	y	r	y	y	c	y	b	$H_2CO_3(CO_2 \text{ at } 1 \text{ atm.})$
$10^{-5}$	$10^{-9}$	5	v	y	b	g	r	y	y	c	y	b	0.2 M- $NH_4Cl$
$10^{-6}$	$10^{-8}$	6	v	y	b	b	r	y	y	c	y	b	
$10^{-7}$	$10^{-7}$	7	v	y	b	b	t	g	y	c	y	b	"Neutral point"
$10^{-8}$	$10^{-6}$	8	v	y	b	b	b	b	y	c	y	b	1 M- $NaHCO_3$
$10^{-9}$	$10^{-5}$	9	v	y	b	b	b	b	g	t	y	b	0.2 M- $NaC_2H_3O_2$
$10^{-10}$	$10^{-4}$	10	v	y	b	b	b	b	b	r	y	b	
$10^{-11}$	$10^{-3}$	11	v	y	b	b	b	b	b	r	o	b	0.05 M- $NH_4OH$ ;
$10^{-12}$	$10^{-2}$	12	v	y	b	b	b	b	b	r	r	b	0.4 M- $Na_2CO_3$
$10^{-13}$	$10^{-1}$	13	v	y	b	b	b	b	b	r	r	g	0.1 M- $NaOH$
$10^{-14}$	1	14	v	y	b	b	b	b	b	r	r	y	1 M- $NaOH$

(Abbreviations: b = blue, c = colorless, g = green, o = orange, r = red, y = yellow, v = violet, t = transition.)

\* pH is an abbreviated designation of the concentration of  $H^+$  much used in biological work. Its meaning is obvious from the table.

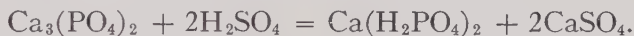
**13.** The concentration of  $H^+$  and  $OH^-$  in a solution may be estimated approximately by the aid of indicators (see page 76). Table 2 gives the concentrations of  $H^+$  and  $OH^-$  between normal  $H^+$  and normal  $OH^-$ , together with the corresponding colors shown by several of the common indicators. The colors given are approximate only, depending not only on hydrogen ion concentration, but also on indicator concentration, other ions, vessel size, illumination, and visual peculiarities. Where accuracy is desired, the indicator should be used only to compare an unknown solution with one of known hydrogen ion concentration under identical conditions of the above factors.

**14. Ionization of Weak Acids, Bases and Salts.** The fact that many acids, bases and salts are but slightly ionized, as set forth in Chapter VIII, furnishes other reasons for expecting certain reactions to take place, for the principles of equilibrium tell us that in such cases the corresponding ions will unite, when brought together, to an extent depending on the ionization of the substance. For example, because we know that acetic acid is weak, that is, but slightly ionized, we know that when hydrochloric acid, which gives a high concentration of  $H^+$ , is mixed with sodium acetate, which gives a high concentration of  $C_2H_3O_2^-$ , these ions will combine till one or both are almost used up. Although sodium acetate is not a base, but a salt, we see that it has the effect of reducing high acidity. Similarly, because  $NH_4OH$  is a weak base it can be prepared from any ammonium salt by the action of any strong base, since  $NH_4^+$  and  $OH^-$  unite rather completely. This property is used as a test for  $NH_4^+$ , and also in the manufacture of  $NH_3$ . Considerable ammonia is given off when coal is distilled, as in making gas and coke. This is extracted from the gas by washing in sulfuric acid, forming  $(NH_4)_2SO_4$ . When this salt is acted upon by slaked lime,  $Ca(OH)_2$ , which gives a sufficiently high concentration of  $OH^-$ , there is set free  $NH_4OH$ , which breaks up at the temperature



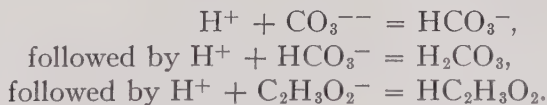
applied into  $\text{NH}_3$  gas and  $\text{H}_2\text{O}$ . It is evident, in general, that weak acids should be liberated from their salts in solution by the action of stronger acids, and that weak bases should be liberated in like manner by strong bases.

**15.** An important application of this principle is in making "super-phosphate" for fertilizer. Tri-calcium phosphate (normal calcium phosphate),  $\text{Ca}_3(\text{PO}_4)_2$ , occurs in bones and mineral deposits, but is so insoluble that even though finely ground it does not furnish plants at all freely with the phosphate necessary for their growth. Accordingly the soluble calcium dihydrogen phosphate is produced by the action of concentrated sulfuric acid, as represented by the equation,



Enough lime is then added to change the dihydrogen to the monohydrogen phosphate,  $\text{CaHPO}_4$ .

**16.** Where the ions of several weak acids are competing for an insufficient amount of hydrogen ion, it is evident that the weakest acid will be formed first, the next weakest second, etc. In a mixture of  $\text{C}_2\text{H}_3\text{O}_2^-$  and  $\text{CO}_3^{--}$ , the values on page 113, or page 161, make it evident that if  $\text{H}^+$  is added to the solution gradually, the first reaction to take place will be



**17. Complex Ions.** As a rule the positive ions in solution are very simple, consisting nearly always only of a metallic atom, with its ionic charge or charges. There are, however, some cases where these simple ions can unite with other ions or neutral molecules and still remain in solution as a more **complex ion**. They may best be considered in groups, according to the substances which are prone to form them.

**18. Ammonia Complexes.** A solution of ammonia in water yields all of the substances denoted in the equation,



Ordinarily, when this solution is added to one containing an ion of a heavy metal, there is enough  $\text{OH}^-$  present to precipitate the metallic hydroxide. If, however, more of the ammonia solution is added, the concentration of  $\text{NH}_3$  will increase faster than that of  $\text{OH}^-$ , and there results, in the case of certain metallic ions, notably  $\text{Cu}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Ag}^+$  and  $\text{Cu}^+$ , a solution which contains a complex positive ion containing both metal and ammonia. With the divalent cations the complex ions seem all to contain  $4\text{NH}_3$ , while those of the mono-valent ions contain  $2\text{NH}_3$ , so that the formulas are as follows:  $\text{Cu}(\text{NH}_3)_4^{++}$ ,  $\text{Ni}(\text{NH}_3)_4^{++}$ ,  $\text{Cd}(\text{NH}_3)_4^{++}$ ,  $\text{Ag}(\text{NH}_3)_2^+$ ,  $\text{Cu}(\text{NH}_3)_2^+$ . Since the  $\text{NH}_3$  is a neutral molecule its presence does not alter the original ionic charge. In the cases of copper and nickel, these ammonia complexes are a deep blue in color, furnishing rather delicate tests for the presence of these metals. On account of this behavior the effect of an excess of ammonia is always to use up most of the free ions of these metals, with corresponding effects upon other equilibria, as will be explained later.

**19. Cyanide Complexes.** Cyanide ion has the power to form complexes with a large number of metallic ions. In this case the metals are contained in the anion as illustrated by the equation for the formation of the silver cyanide complex ion:



(When  $\text{Ag}^+$  is present in any considerable amount,  $\text{AgCN}$  is first precipitated, dissolving in excess of  $\text{CN}^-$ .)

Among these complexes may be mentioned the following:



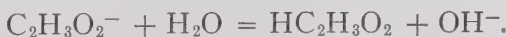


**20. Complex Halides.** Many metallic ions, especially those of the noble metals, have a tendency to form complex halides. This is particularly strong in the case of gold, platinum and the other "platinum metals," as shown in the following:  $\text{AuCl}_2^-$ ,  $\text{AuCl}_4^-$ ,  $\text{PtCl}_6^{--}$ .

**21. Complex Oxalates.** Certain metallic ions form complex oxalates with oxalate ion,  $\text{C}_2\text{O}_4^{--}$ , as exemplified by  $\text{Fe}(\text{C}_2\text{O}_4)_3^{---}$ .

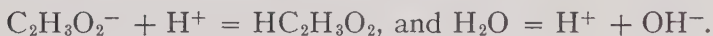
**22. Competition between the Foregoing Factors.** We have seen, in a few instances, how reactions are determined by competition between the various ions of weak acids, or the relative solubilities of various salts of the same ion. We are now prepared to discuss competition between the different factors, volatility, solubility, ionization of water, weak acids, bases and salts, complex ions, and to consider general examples of the control of reactions.

**23. Hydrolysis.** When the salt of a weak acid is dissolved in water we have present in the solution an ion that has a great tendency to combine with hydrogen ion. Now water, though it is such a weak electrolyte, yields some hydrogen ion. Consequently, there is a slight formation of the weak acid, with a resulting decrease in the concentration of the hydrogen ion and a corresponding increase in the concentration of the hydroxide ion. To say this concretely, let us consider a solution of sodium acetate, which gives a large concentration of  $\text{Na}^+$  and  $\text{C}_2\text{H}_3\text{O}_2^-$ . Now, since the water yields a trace of  $\text{H}^+$  and  $\text{OH}^-$ , and since  $\text{HC}_2\text{H}_3\text{O}_2$  is a weak acid, there will be some union of  $\text{H}^+$  and  $\text{C}_2\text{H}_3\text{O}_2^-$  to form the acid, liberating an excess of  $\text{OH}^-$ , so that the solution will be slightly alkaline. This may be expressed by an equation as follows:



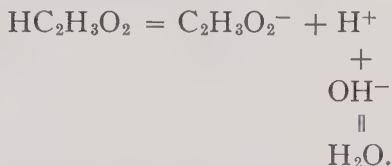
It will be observed that this reaction is the reverse of the neutralization of acetic acid with a strong base, and since the latter reaction is nearly complete, of course the former can take place but slightly under similar conditions.

In writing the equation we show the net effect of what has happened, as expressed previously in words. We must guard against the error of thinking that the formulas on the right-hand side of the equation tell what is in the solution after equilibrium is reached. The solution still contains mostly  $\text{C}_2\text{H}_3\text{O}_2^-$  and  $\text{H}_2\text{O}$ , which fact is expressed by saying that the above substances react only slightly before equilibrium is reached, not by writing their formulas on both sides of the equation. Moreover, in a single equation like this, we should not write water as ionized, for the bulk of it is un-ionized. As a matter of fact, there are two simultaneous reactions occurring, as follows:



The sum of these two gives the former.

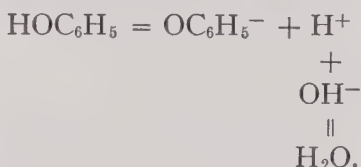
Obviously there is a competition between  $\text{C}_2\text{H}_3\text{O}_2^-$  and  $\text{OH}^-$  for the  $\text{H}^+$ , as might be represented in this way:



That the  $\text{OH}^-$  should get or keep most of the  $\text{H}^+$  is to be expected from the fact that water is vastly less ionized than is acetic acid. It is this disparity between the ionization of the two substances that enables  $\text{C}_2\text{H}_3\text{O}_2^-$  to set free but a slight amount of  $\text{OH}^-$  from water, on the one hand, and which causes neutralization of  $\text{HC}_2\text{H}_3\text{O}_2$  by  $\text{OH}^-$  to be nearly complete, on the other hand.

**24.** If, instead of an acetate, we dissolve in the water the salt of some weaker acid, like sodium phenolate,  $\text{NaOC}_6\text{H}_5$

(the "phenol sodique" of the drug store), we have in phenolate ion,  $\text{OC}_6\text{H}_5^-$ , one which will unite with the hydrogen ion of water more completely than will acetate ion, forming  $\text{HOC}_6\text{H}_5$ , the acid known as phenol, or carbolic acid, and setting free from the water more  $\text{OH}^-$  than in the case of sodium acetate. The competition for  $\text{H}^+$  is here between  $\text{OH}^-$  and  $\text{OC}_6\text{H}_5^-$ , and though the latter gets but little of it, since carbolic acid is much more ionized than water, it nevertheless gets more than does acetate ion. We may express this competition in the same manner as before,

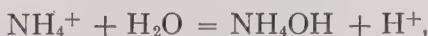


The net result we may write, as before,



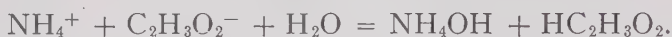
The discussion shows why "phenol sodique" can be used as a mild antiseptic. Its solution always contains free carbolic acid, which is an antiseptic, and though its concentration is small, if it is used up more can be formed from the above equilibrium to replace it.

**25.** A process such as this is called hydrolysis. The idea underlying the name is that a salt is split up by water into free acid and base. We see that salts of weak acids always hydrolyze in aqueous solution on account of the possibility of forming the free weak acid. Of course, the ions giving weak bases also take part in hydrolysis. All ammonium salts are hydrolyzed, because of the formation of the weak base, ammonium hydroxide, as illustrated by the equation,



where the solution becomes slightly acid. If the salt is one

of both a weak acid and a weak base, like ammonium acetate,  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ , both of its ions take part in hydrolysis, as shown by the equation,



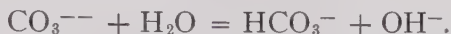
In a case like this the acidity or alkalinity of the resulting solution depends upon whether the acid or the base is weaker. In this case they are of almost identical strength, as may be seen from the values on page 161, so that the solution is almost neutral, though it does contain more  $\text{NH}_4\text{OH}$  than a solution of  $\text{NH}_4\text{Cl}$ , and more free  $\text{HC}_2\text{H}_3\text{O}_2$  than one of  $\text{NaC}_2\text{H}_3\text{O}_2$ , since both of the ions present aid in splitting up the water.

**26.** An alternate point of view regarding  $\text{NH}_4^+$  is to consider it, itself, as a weak acid, dissociating as follows:  $\text{NH}_4^+ = \text{NH}_3 + \text{H}^+$ . This has certain advantages in simplicity of representation, although it is not essentially different from  $\text{NH}_4^+ + \text{H}_2\text{O} = \text{NH}_4\text{OH} + \text{H}^+$ , for both  $\text{NH}_3$  and  $\text{H}^+$  are "hydrated."

**27.** Hydrolysis plays an important part in many reactions, a few examples of which will be given. It is desirable that solutions to be used for household cleaning should have a slightly alkaline reaction, since this aids in emulsifying grease and removing dirt, and also tends to soften hard water, as will be explained later. It is not desirable, however, to use a strong base like sodium hydroxide, because this gives too great a concentration of  $\text{OH}^-$ , which has injurious effects on the hands and on some fabrics, unless used in very dilute solution, where the slight amount of  $\text{OH}^-$  would soon be used up. What is wanted is a solution containing but little free  $\text{OH}^-$ , but which is able to yield more should this be used up. Such is the case with ammonia, so that it finds large use in the home. We see also that salts of weak acids fulfill these conditions, and several of them find extensive application as cleansing agents. Sodium carbonate,  $\text{Na}_2\text{CO}_3$ , is the salt of a very weak acid,



and its solutions give a very marked alkaline reaction, as follows:



On this account it is extensively known and used as "washing soda." There are two sodium carbonates, this one and  $\text{NaHCO}_3$ , sodium acid carbonate. The solution of the latter also undergoes hydrolysis,



However, since  $\text{H}_2\text{CO}_3$  is considerably more dissociated than  $\text{HCO}_3^-$ , according to the figures given on page 161, the former will be formed from  $\text{HCO}_3^-$  and  $\text{H}^+$  less completely than the latter will be from  $\text{CO}_3^{--}$  and  $\text{H}^+$ . Hence the solution of  $\text{Na}_2\text{CO}_3$  is much more alkaline than one of  $\text{NaHCO}_3$ , and is used as "washing soda," whereas the latter is used only where a much less alkaline reaction is desired, as for internal use. The  $\text{NaHCO}_3$ , on the other hand, is "baking soda," because it can yield much more  $\text{CO}_2$  for the same weight both of itself and acid.

**28.** Borax, sodium borate, is the salt of the very weak boric acid, and has the same effect in cleansing as sodium carbonate. Sodium silicate, the salt of weak silicic acid, behaves in the same way, and is a constituent of laundry soaps.

**29.** Aluminum hydroxide,  $\text{Al}(\text{OH})_3$ , is not only insoluble, but is a weak base as well, so that aluminum ion,  $\text{Al}^{+++}$ , in water forms some of the hydroxide, liberating the hydrogen ion and causing the solution to become distinctly acid. On this account aluminum salts can be used to liberate carbon dioxide from carbonates, as is done in the alum baking powders. A similar reaction is used by oil companies in a scheme for extinguishing gasoline or petroleum fires on oil tanks. The sodium carbonate solution and one of aluminum sulfate, containing glue to produce a froth which retains the  $\text{CO}_2$  gas, are projected from adjacent pipes over the

burning tank, when the froth produced spreads over the fire and quenches it.

**30.** Due to hydrolysis of aluminum ion with ions of very weak acids, aluminum salts of these cannot exist in the presence of water. When  $\text{CO}_3^{--}$  is added to  $\text{Al}^{+++}$ ,  $\text{Al}(\text{OH})_3$  is precipitated instead of a carbonate; and aluminum sulfide, prepared directly from the elements, when put into water, decomposes completely as follows:



**31.** There are a number of other compounds, such as the chlorides of the non-metals, that undergo complete hydrolysis. When  $\text{PCl}_3$ , phosphorus tri-chloride, is put into water the following reaction takes place:



The hydroxide of phosphorus is so completely an acid rather than a base that the above reaction is complete.

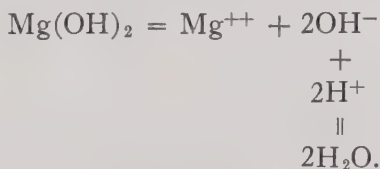
**32.** In titrating a weak acid with a strong base, or vice versa, it is necessary to determine, not when the solution is neutral, but when it contains equivalent amounts of acid and base, a minute proportion of which will be free, giving an alkaline or acid reaction, as the case may be. If sodium acetate, for example, is dissolved in water, the solution is slightly alkaline, although equivalent amounts of acid and base are present. To reproduce this condition, when acetic acid is titrated with sodium hydroxide, one should use an indicator like phenolphthalein, which, as shown on page 171, changes color in a solution which is faintly alkaline, so that a slight excess of either acid or base would affect the indicator. Similarly, in titrating ammonia with hydrochloric acid, we wish to end with the solution not really neutral but slightly acid, since a solution of ammonium chloride reacts slightly acid. Hence an indicator like methyl orange, according to the table on page 171, would be suitable for this purpose. In general, the proper indicator to use in a

titration may be found by taking the normal salt which will result from the titration, dissolving it in water and determining what indicator will change color when a drop of solution of the free acid or base is added in excess.

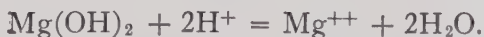
**33. The Solution of Hydroxides.** We have seen that when a more or less insoluble metallic hydroxide is in contact with water it gives to the water a certain amount of its ions, equilibrium being reached the sooner the less soluble the hydroxide. As an example we may consider magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ , which gives a small concentration of ions as follows:



We have seen also that hydrogen ion has a very great tendency to unite with hydroxide ion. If, therefore,  $\text{H}^+$  is added to the precipitate of magnesium hydroxide suspended in water, there will be a competition between the  $\text{H}^+$  and the  $\text{Mg}^{++}$  for the  $\text{OH}^-$ , which may be represented, as before, by the double equation,



Now, since water is so extremely undissociated we might expect that the  $\text{H}^+$  added would be successful in stealing the  $\text{OH}^-$  away from the magnesium ion, liberating the latter, which would thus go into solution so that the effect of the acid would be to dissolve the precipitate. The total reaction is therefore



As a matter of fact, water is formed so completely from its ions that it takes but a moderate concentration of acid to dissolve practically all hydroxides.

**34.** Our principles of equilibrium would lead us to expect that any substance that would unite with  $\text{OH}^-$  would have the effect of dissolving insoluble bases. Besides  $\text{H}^+$ , we have found that  $\text{NH}_4^+$  is a substance which has a tendency to unite with  $\text{OH}^-$  to form the weak base  $\text{NH}_4\text{OH}$ . We know, however, that these two ions do not unite nearly so completely as do  $\text{H}^+$  and  $\text{OH}^-$ , therefore we should not expect  $\text{NH}_4^+$  to be nearly as effective as  $\text{H}^+$  in dissolving bases. It is true that the solubility of any base will be increased by the presence of  $\text{NH}_4^+$ , but if the base is very insoluble to begin with, the increase may not be sufficient to bring the amount in solution up to a value such that we would call it soluble. Suppose, for example, that the solubilities of two bases in water are 0.001 and 0.000001 molal respectively, and that the addition of a certain amount of  $\text{NH}_4^+$  is enough to increase each 1000 times. The effect would be to make the solubilities of the two bases now 1 molal and 0.001 molal, respectively. We would then call the first soluble in  $\text{NH}_4^+$ , but the second, insoluble. Among the insoluble bases which may be thus dissolved in  $\text{NH}_4^+$  are  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_2$ ,  $\text{Mn}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ .

**35. The Solution of Oxides.** Oxides of metals are much like the corresponding hydroxides, and may either be converted into hydroxides, in some cases, or produced from them by heating. The solubility of hydroxides in  $\text{H}^+$  leads us to expect that oxides will likewise dissolve in acids. We may think here of the formation of water from the  $\text{H}^+$  of the acid and the oxygen of the oxide. Most oxides, indeed, are easily dissolved in acids, though more difficultly than are the corresponding hydroxides. This difficulty may be largely a matter of the speed of the reaction. In a few instances, notably  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$ , if they have been heated to a very high temperature they become practically insoluble in acids.

**36. Amphoteric Hydroxides.** There are several metallic hydroxides that are capable of acting either as weak bases

or weak acids. Any substances that behave in this way are called **amphoteric**. Such a substance may give to water not only the metallic cation and the  $\text{OH}^-$  of a base, but also  $\text{H}^+$  and a corresponding anion. Taking  $\text{Al}(\text{OH})_3$  as an example, we may express this double power of dissociating as follows:



As is the case with most weak polybasic acids, the various hydrogen ions dissociate in steps, and since  $\text{H}_3\text{AlO}_3$  is an exceedingly weak acid, even the first  $\text{H}^+$  is ionized with difficulty, and the second and third are practically unionized unless a large excess of  $\text{OH}^-$  is added. From the double equilibrium that we have represented it will be seen that the precipitate can be dissolved not only by the addition of  $\text{H}^+$ , which would act as follows:



but also by the addition of  $\text{OH}^-$ , which would act in the following way,



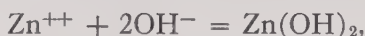
It is possible, therefore, to have aluminum present either in an alkaline or in an acid solution, while in a solution approximately neutral it cannot exist, but will be precipitated as  $\text{Al}(\text{OH})_3$ .

**37.** Other hydroxides behaving in this way are those of zinc, chromium, lead and tin (both stannous and stannic). This amphoteric character may be made use of in separating from each other metallic ions existing in the same solution. Thus  $\text{Fe}^{+++}$  is commonly separated from  $\text{Al}^{+++}$  and  $\text{Cr}^{+++}$  by adding concentrated  $\text{OH}^-$  in excess, which leaves the first precipitated as  $\text{Fe}(\text{OH})_3$ , but dissolves the others as aluminate and chromite ions respectively.

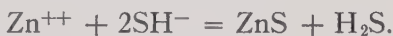
**38. The Iso-electric Point** is the hydrogen ion concentration at which an amphoteric substance is least ionized in

both directions. If it is a relatively insoluble substance, its solubility would be at a minimum at that point. If its acid and basic strengths are equal, then the iso-electric point is at  $(\text{H}^+) = (\text{OH}^-) = 10^{-7}$ . If its acid strength is greater than its basic strength, a higher concentration of  $\text{H}^+$  is necessary to repress the acid ionization and the iso-electric point will be at  $(\text{H}^+) > 10^{-7}$ .

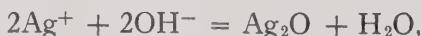
**39. The Solution of Sulfides in Hydrogen Ion.** The similarity between oxides and sulfides has been previously pointed out, also the fact that hydrogen sulfide is a very weak electrolyte, like water. It is but a slight transition, therefore, from the consideration of oxides to that of sulfides. The chief difference to be noted is that whereas reactions like the following are very numerous,



the corresponding reaction, when sulfur is substituted for oxygen, is the formation of a sulfide, rather than a hydro-sulfide, as shown by the reaction:



This is analogous to what takes place with  $\text{OH}^-$  in the case of  $\text{Ag}^+$ , and, when the solution is boiled, with  $\text{Cu}^{++}$ , as shown by

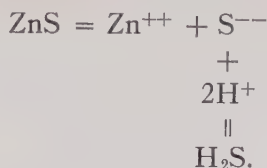


and



The solution of a sulfide in an acid depends upon the removal of the sulfide ion by the hydrogen ion of the acid to form hydrogen sulfide,  $\text{H}_2\text{S}$ , and its precipitation depends upon the presence of sufficient sulfide ion. This competition between the metallic ion and the hydrogen ion for the sulfide ion may be represented by the scheme used before,





**40.** Some sulfides are so insoluble that the metallic ion finds enough sulfide ion to be precipitated even when the solution contains a moderately concentrated acid. These sulfides, conversely, will not be dissolved by hydrogen ion in moderate concentrations. The sulfides which behave in this way include  $\text{Ag}_2\text{S}$ ,  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ ,  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{S}_5$ . Next, we have several, including  $\text{CdS}$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_5$ ,  $\text{SnS}$ ,  $\text{SnS}_2$ , that will dissolve if the  $\text{H}^{+}$  is concentrated but not if it is dilute. Then follow  $\text{ZnS}$ ,  $\text{MnS}$ ,  $\text{FeS}$ ,  $\text{NiS}$ ,  $\text{CoS}$ , which are so soluble that dilute  $\text{H}^{+}$  is sufficient to prevent their precipitation. The cases of  $\text{NiS}$  and  $\text{CoS}$  are peculiar in that they are not precipitated in acid solution, but nevertheless will not dissolve at all rapidly in dilute acid if first precipitated from an alkaline solution. This may be due to the existence of two modifications of the solids, so that when the more soluble modification is once precipitated it changes over into the insoluble modification; or it may be an example of slow rate of reaction, similar to the slow reaction between certain acids and oxides, referred to on page 182. In order to precipitate this group of sulfides it is necessary to have a neutral or slightly alkaline solution so that sufficient sulfide ion can be present. The usual reagent is a solution of ammonium sulfide, made by passing  $\text{H}_2\text{S}$  into  $\text{NH}_4\text{OH}$  solution. If acetic acid is used, it is possible, by adding acetate ion, to reduce the concentration of  $\text{H}^{+}$  sufficiently to allow the precipitation of  $\text{ZnS}$ .

**41.** Another factor that may be used to assist the solution of a sulfide is the volatility of  $\text{H}_2\text{S}$ . If the solution is boiled, the  $\text{H}_2\text{S}$  is more readily removed, so that more can form, resulting in an easier and more rapid solution of the

sulfide. To dissolve the less soluble sulfides the use of concentrated  $H^+$ , together with boiling the solution, is insufficient, and we shall see in Chapter XV that it is necessary to destroy the  $H_2S$  by an oxidizing agent.

The order of solubility of the above sulfides in water is roughly as follows, beginning with the most soluble:  $MnS$ ,  $FeS$ ,  $ZnS$ ,  $NiS$ ,  $CoS$ ,  $SnS_2$ ,  $SnS$ ,  $Sb_2S_3$ ,  $CdS$ ,  $PbS$ ,  $Bi_2S_3$ ,  $CuS$ ,  $Ag_2S$ ,  $As_2S_5$ ,  $HgS$ .

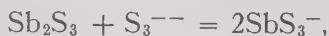
**42. Amphoteric and Acid Sulfides.** We have seen above how several hydroxides are able to dissolve in  $OH^-$ . There are, likewise, five sulfides which can dissolve in either  $OH^-$  or  $SH^-$ , namely,  $As_2S_3$ ,  $As_2S_5$ ,  $Sb_2S_3$ ,  $Sb_2S_5$ ,  $SnS_2$ .

The analogy between the oxides and sulfides may be brought out in the following parallel reactions:



The oxide may be dissolved in  $SH^-$  and the sulfide in  $OH^-$  to produce mixtures of the above products or else intermediate ions.

The compounds in which the metals have the lower oxidation number are always less acidic, both in the case of the oxides and the sulfides, hence  $Sb_2S_3$  dissolves with some difficulty in ammonium sulfide, and  $SnS$  is practically insoluble in the same. In dissolving both of these sulfides yellow ammonium sulfide is used, which contains polysulfide ions, such as  $S_2^{--}$ ,  $S_3^{--}$ , etc. Although these ions are usually written in this way for the sake of simplicity, they are actually ions of weak acids and it would be doubtless more accurate to write:  $HS_2^-$ ,  $HS_3^-$ , etc. This is capable of dissolving the lower sulfides of all three metals, changing them to the sulfo-ion of the higher valence, thus,



When acid is added to the solutions of the above sulfo-

ions the weak acid,  $\text{H}_2\text{S}$ , is produced, reprecipitating the sulfides, just as the addition of acid to stannate ion reprecipitates the stannic hydroxide. This reprecipitation consists simply in the reversal of the reactions whereby these sulfones are produced.

The different behaviors of sulfides towards the  $\text{H}^+$  and  $\text{SH}^-$  or  $\text{S}_2^{--}$  is made the basis of important separations in both qualitative and quantitative analysis. If a solution contains the following ions,  $\text{Pb}^{++}$ ,  $\text{Bi}^{+++}$ ,  $\text{Cu}^{++}$ ,  $\text{As}^{+++}$ ,  $\text{Sb}^{+++}$ ,  $\text{Sn}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Mg}^{++}$ , they can be divided into groups by controlling the concentrations of the substances in the equilibrium,

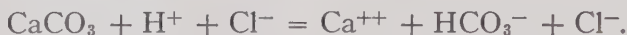


This separation can best be outlined by the aid of a diagram.

Have dilute $\text{H}^+$ (0.3 <i>M</i> -HCl) present, and pass in $\text{H}_2\text{S}$			
Precipitate insoluble $\text{PbS}$ , $\text{Bi}_2\text{S}_3$ , $\text{CuS}$ , $\text{As}_2\text{S}_3$ , $\text{Sb}_2\text{S}_3$ , $\text{SnS}$ . Treat with $\text{S}_2^{--}$ (yellow ammonium sulfide)		In solution $\text{Zn}^{++}$ , $\text{Mn}^{++}$ , $\text{Mg}^{++}$ . Make alkaline, add $\text{S}^{--}(\text{SH}^-)$ (ammonium sulfide)	
Left insoluble, $\text{PbS}$ , $\text{Bi}_2\text{S}_3$ , $\text{CuS}$ .	In solution $\text{AsS}_3^-$ , $\text{SbS}_3^-$ , $\text{SnS}_3^{--}$ . Reprecipitate the sulfides and heat with 12 <i>N</i> -HCl		Precipitate $\text{ZnS}$ , $\text{MnS}$
	Left insoluble, $\text{As}_2\text{S}_5$	In solution $\text{Sn}^{+++}$ , $\text{Sb}^{+++}$ , dilute to 2 <i>N</i> - $\text{H}^+$ , pass in $\text{H}_2\text{S}$ cold, ppt. $\text{Sb}_2\text{S}_3$	
		In solution $\text{Mg}^{++}$	

**43. Salts of Other Weak Acids.** Salts of all weak acids are made more soluble by the addition of  $\text{H}^+$ . This increase in solubility, in the case of carbonates, is enough to bring all insoluble carbonates into solution in dilute  $\text{H}^+$ . A very interesting case of the solution of a carbonate was alluded to on page 148. It is the reaction whereby hard water is pro-

duced from limestone rock. If very dilute  $\text{H}^+$ , as is present in very dilute  $\text{HCl}$ , is allowed to act upon  $\text{CaCO}_3$ , the  $\text{CO}_3^{--}$  which the latter gives to the solution in very slight amount is converted into  $\text{HCO}_3^-$  only, and not into  $\text{H}_2\text{CO}_3$ , as would be the case if more concentrated acid were used. The equation for this reaction is as follows:



If  $\text{H}_2\text{CO}_3$  is used instead of  $\text{HCl}$ , it also can furnish sufficient  $\text{H}^+$  to bring about essentially the same reaction,



Since most surface water contains some dissolved carbon dioxide, the above reaction takes place whenever such water flows over limestone. A quite analogous reaction occurs with  $\text{MgCO}_3$ . The reaction can be reversed by removing the  $\text{H}_2\text{CO}_3$ , either by boiling the solution, as occurs in a tea-kettle, whence the name "temporary hardness," or else by neutralizing it with some alkali, or some substance giving  $\text{OH}^-$  by hydrolysis, like sodium carbonate or borax. When this is done on a large scale, the water is analyzed and just the right amount of  $\text{Ca}(\text{OH})_2$  is added. Although more  $\text{Ca}^{++}$  is added in this way, there is produced enough  $\text{CO}_3^{--}$  to precipitate all of it; the total reaction is represented by the equation:



When the hardness in water is produced by dissolving a salt like  $\text{CaSO}_4$ , it is necessary to add  $\text{CO}_3^{--}$  (as  $\text{Na}_2\text{CO}_3$ ) to precipitate the  $\text{Ca}^{++}$ .

**44.** When the solubility of the hydroxide of a metal is about as small as the solubility of its carbonate, the latter will hydrolyze partly to give a basic carbonate. This is the case with the carbonates of copper, lead and mercury, as illustrated by  $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$ , the "white lead" of the painter.

**45.** There are no phosphates so insoluble in water but that they are dissolved by moderately concentrated  $H^+$ . Although  $PO_4^{---}$  is the ion of the very weak acid,  $HPO_4^{--}$ , nevertheless dilute  $H^+$  is not sufficient to dissolve all of the normal phosphates, both because some are so insoluble to begin with that the increase is not sufficient to make them soluble in the usual sense, and also because some monohydrogen phosphates, like  $CaHPO_4$ , are rather insoluble, and even though  $Ca_3(PO_4)_2$  be converted into the former, solution does not result.

**46.** As a rule the acid salts are more soluble than the normal salts, as exemplified by the series of calcium phosphates.  $Ca(H_2PO_4)_2$  is soluble,  $CaHPO_4$  is insoluble and  $Ca_3(PO_4)_2$  is very insoluble in water. The chief exception to this rule is furnished by the sodium carbonates, where the acid salt is the less soluble.

**47.** The industrial preparation of sodium carbonate by the Solvay process furnishes an interesting application of the principles here discussed. The normal salt,  $Na_2CO_3$ , is very soluble, but the acid salt,  $NaHCO_3$ , is not very soluble in the cold. The latter can therefore be precipitated by bringing together the ions  $Na^+$  and  $HCO_3^-$  in sufficient concentration. To do this,  $NH_3$  gas and  $CO_2$  gas are led into a cold concentrated solution of  $NaCl$ . The acid and base produced by the solution of the gases in water react to give  $NH_4^+$  and  $HCO_3^-$ , provided they are used in the right proportion, and when the concentration of  $HCO_3^-$  reaches a sufficient value it begins to precipitate the  $Na^+$  as  $NaHCO_3$ .<sup>1</sup>

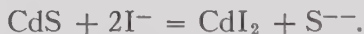
**48. Solution by Forming Weak Salts.** In the previous cases we have treated compounds which could be brought into solution by adding some substance, especially  $H^+$ , which would use up the anion of the precipitate. It is

<sup>1</sup> This solid is separated from the solution and heated to produce  $Na_2CO_3$  (cf. paragraph 56). The  $CO_2$  given off during the heating is returned to the process. A fresh supply is obtained by heating  $CaCO_3$ ; the  $CaO$  resulting is slaked to give  $Ca(OH)_2$ , which is used to recover the  $NH_3$  from the  $NH_4^+$ .

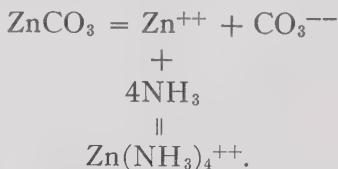
equally possible to dissolve a compound by adding some reagent that will use up the free cation. Thus lead sulfate,  $\text{PbSO}_4$ , may be dissolved by the addition of an acetate, because lead acetate is a soluble weak salt, and the acetate ion, if in sufficient concentration, can compete successfully with the sulfate ion for the lead ion, as shown by the equation,



Similar effects are shown, at least to some extent, wherever weak salts, such as are mentioned on page 114, can be formed. We find, for example, that  $\text{CdI}_2$  is a moderately weak salt; consequently the following reaction can be made to proceed to some extent by using a sufficient concentration of  $\text{I}^-$ :



**49. Solution by Forming Complex Ions.** Wherever the cation is capable of forming a complex ion, a precipitate can be rendered more soluble than it is in water. Thus, a salt like  $\text{ZnCO}_3$  can be dissolved, not only by using up the anion, as in adding  $\text{H}^+$ , but also by using up the cation, as when  $\text{Zn}(\text{NH}_3)_4^{++}$  is formed by the addition of ammonia solution. The competition between the  $\text{CO}_3^{--}$  and the  $\text{NH}_3$  may be represented as before:

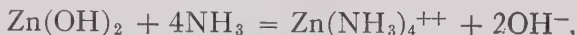


If the concentration of the ammonia is sufficient, the complex ion is formed at the expense of the insoluble carbonate, resulting in the net reaction,





It is worth noting that the solution of  $\text{Zn(OH)}_2$  in  $\text{NH}_3$  (aq.), by the reaction:



would be assisted by  $\text{NH}_4^+$ , if present, reacting with the  $\text{OH}^-$ , giving a net reaction of:



In the case of  $\text{ZnS}$ , which is much less soluble, the formation of the complex ion cannot take place to an appreciable extent, so that  $\text{ZnS}$  is not dissolved by ammonia. The copper ammonia complex ion seems to be formed more completely than the corresponding zinc ion, so that traces of  $\text{Cu(NH}_3)_4^{++}$  can be formed from  $\text{CuS}$  if concentrated ammonia is used, in spite of the smaller solubility of  $\text{CuS}$ .

#### 50. Solution by Forming Ions of Amphoteric Hydroxides.

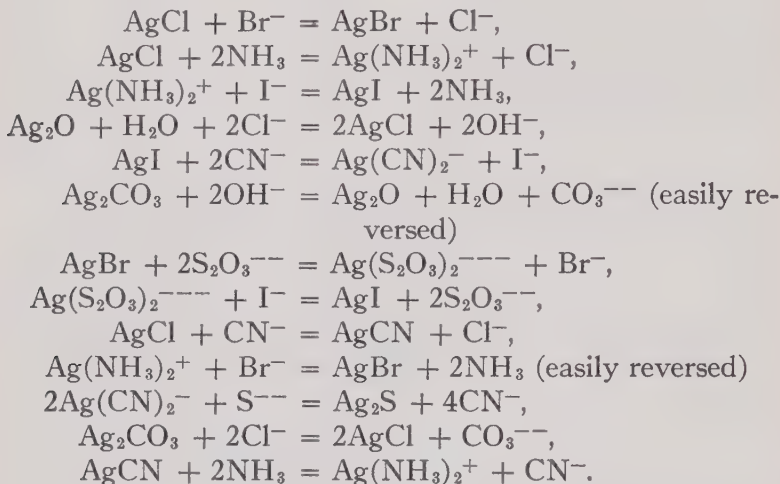
The effect of a considerable concentration of  $\text{OH}^-$  may be to dissolve the relatively insoluble salts of certain metals, in a fashion similar to that whereby complex ions are formed. In fact, these ions may be considered as complex ions. Most of the lead salts, for example, are dissolved by  $\text{OH}^-$ , as exemplified by the reaction,



Even  $\text{ZnS}$  is not so insoluble but that it can be dissolved by concentrated  $\text{OH}^-$ .

**51. Systematizing the Reactions of a Given Ion.** It is not necessary to perform and remember all of the reactions of a certain ion with a set of reagents in order to tell what they will be. It suffices to make an intelligent selection of a few of the possible reactions and arrange the resulting information systematically. As an example of what is meant let us consider a number of the reactions of silver ion,  $\text{Ag}^+$ , with the following:  $\text{CO}_3^{--}$ ,  $\text{OH}^-$ ,  $\text{CN}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{S}^{--}$ ,  $\text{NH}_3$ ,  $\text{S}_2\text{O}_3^{--}$ . Let us assume that we have performed experiments which show that the reactions take place which are

represented by the following equations as read from left to right:



From these observations it is possible to arrange the following list of substances in the order showing the completeness with which they unite with  $\text{Ag}^+$  to form a precipitate or a complex ion as the case may be. It must be understood that the reagents forming complexes are taken in moderate excess:

REAGENT	TO FORM
$\text{CO}_3^{--}$	$\text{Ag}_2\text{CO}_3$
$\text{OH}^-$	$\text{Ag}_2\text{O}$
$\text{Cl}^-$	$\text{AgCl}$
$\text{CN}^-$	$\text{AgCN}$
$\text{NH}_3$	$\text{Ag}(\text{NH}_3)_2^+$
$\text{Br}^-$	$\text{AgBr}$
$\text{S}_2\text{O}_3^{--}$	$\text{Ag}(\text{S}_2\text{O}_3)_2^{--}$
$\text{I}^-$	$\text{AgI}$
$\text{CN}^-$	$\text{Ag}(\text{CN})_2^-$
$\text{S}^{--}$	$\text{Ag}_2\text{S}$

52. In order to make this list it is necessary to make a minimum of eight observations, and from it it is possible to predict the direction of forty-five reactions. The list

was made in such a way that each substance in the first column will steal  $\text{Ag}^+$  away from its combinations with any substance above it, because less  $\text{Ag}^+$  can exist in the same solution with substances farther down the column than with those higher up at the same concentration. Thus  $\text{AgBr}$  gives to the solution more  $\text{Ag}^+$  than can exist together with  $\text{I}^-$ , hence the following reaction will readily take place:



For the same reason,  $\text{AgI}$  will dissolve in  $\text{CN}^-$ , and also any precipitate in the above list can be transposed into  $\text{AgI}$  by  $\text{I}^-$  except  $\text{Ag}_2\text{S}$ . Where two substances have about the same power to combine with  $\text{Ag}^+$ , as is the case with  $\text{NH}_3$  and  $\text{Br}^-$ , it is possible to reverse the reaction easily by altering the concentrations. Thus the reaction,



can be made to take place as read from left to right or from right to left, according as the concentration of  $\text{NH}_3$  or that of  $\text{Br}^-$ , respectively, is taken in sufficient excess.

By adding to the information given by the above list a few facts about the other reactions of the substances, we are able to predict a very large number of reactions. For example,  $\text{HCN}$  is a very weak acid, hence  $\text{AgCN}$  can be dissolved by  $\text{H}^+$ . For the same reason,  $\text{H}^+$  will liberate  $\text{Ag}^+$  from a solution of  $\text{Ag}(\text{CN})_2^-$ , and if  $\text{Cl}^-$  is present along with the  $\text{H}^+$ , then  $\text{AgCl}$  will be precipitated as follows:



In similar fashion,  $\text{AgCl}$  will be dissolved by  $\text{NH}_3$ , according to the reaction represented earlier, but will be reprecipitated on the addition of  $\text{H}^+$ , which takes up the  $\text{NH}_3$  to form  $\text{NH}_4^+$ , allowing the  $\text{Ag}^+$  to recombine with the  $\text{Cl}^-$  left from the previous reaction, as shown by the equation:



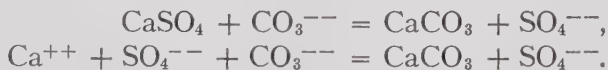
Again, since  $\text{Ag}_2\text{SO}_4$  is moderately soluble (see page 169), we see that it can be readily transposed to  $\text{AgCl}$  by dissolving it in water and adding  $\text{Cl}^-$ , for  $\text{AgCl}$  is insoluble. In order to reverse this transposition we see that some other principle besides solubility must be invoked. If water is absent, we can take advantage of the greater volatility of  $\text{HCl}$  as compared with  $\text{H}_2\text{SO}_4$ , so that the reaction,



can be brought about by heating  $\text{AgCl}$  with concentrated  $\text{H}_2\text{SO}_4$ .

**53. Miscellaneous Transformations.** The general application of the above principles and information can be illustrated by further miscellaneous examples.

To change  $\text{CaSO}_4$  to  $\text{CaCO}_3$  we can take advantage of the greater solubility of the former (see paragraph 9) and treat it with a solution of a soluble carbonate, like  $\text{Na}_2\text{CO}_3$ , which gives  $\text{CO}_3^{--}$ , when the insoluble  $\text{CaCO}_3$  would be precipitated. The manner of expressing this in an equation would depend upon whether the amount of water present is such that the  $\text{CaSO}_4$  is mainly present as solid or as dissolved ions. These cases would be represented respectively as follows:



To bring about the reverse transformation we would have to make up for the greater solubility of  $\text{CaSO}_4$ , which shifts the equilibrium towards  $\text{CaCO}_3$ , by adding  $\text{H}^+$ , which would use up  $\text{CO}_3^{--}$  and reverse the reaction.

**54.** To change  $\text{ZnSO}_4$  to  $\text{ZnCl}_2$  it is necessary to replace  $\text{SO}_4^{--}$  by  $\text{Cl}^-$ . This might be done by adding  $\text{BaCl}_2$  to a solution of the  $\text{ZnSO}_4$ , giving the reaction,



If exactly the right amount of  $\text{BaCl}_2$  were used, all of the

$\text{Ba}^{++}$  and  $\text{SO}_4^{--}$  present would precipitate each other, leaving in solution  $\text{Zn}^{++}$  and  $\text{Cl}^-$ , and if the precipitate were filtered out and the solution evaporated, these ions would combine to give solid  $\text{ZnCl}_2$ , as desired. However, it is difficult to add just the equivalent amount of  $\text{BaCl}_2$ , and it is accordingly better to use a different method, with reagents an excess of which can be easily removed. Since  $\text{Zn}(\text{OH})_2$  is insoluble, it can be precipitated by adding  $\text{OH}^-$  (e.g.,  $\text{NaOH}$  solution) to the solution of  $\text{ZnSO}_4$ . If the precipitate is now filtered out, the  $\text{SO}_4^{--}$  is disposed of. The precipitate of  $\text{Zn}(\text{OH})_2$  can now be dissolved by  $\text{HCl}$  solution, since the  $\text{H}^+$  of the acid unites so strongly with the  $\text{OH}^-$  of the base, giving a solution containing  $\text{Zn}^{++}$ , with  $\text{H}^+$  and  $\text{Cl}^-$  in excess. If, now, this solution is evaporated, the excess of  $\text{H}^+$  and  $\text{Cl}^-$  go off along with the water as  $\text{HCl}$  gas, leaving finally solid  $\text{ZnCl}_2$ . By precipitating the carbonate,  $\text{ZnCO}_3$ , instead of the hydroxide, the same transformation can be made, since  $\text{ZnCO}_3$  is equally soluble in the stronger acids. In fact, a soluble salt of any metal which has an insoluble hydroxide or carbonate can be transposed to another soluble salt of the same metal by precipitation of one of these and dissolving it in the acid corresponding to the desired salt.

**55.** Aluminum chloride,  $\text{AlCl}_3$ , can be changed to aluminum oxide,  $\text{Al}_2\text{O}_3$ , by first precipitating  $\text{Al}(\text{OH})_3$ , using a soluble hydroxide, e.g.,  $\text{NaOH}$ ,  $\text{NH}_4\text{OH}$ , and then heating, which aids the decomposition of the hydroxide into the oxide and the volatile substance steam. The two processes are represented by the equations,

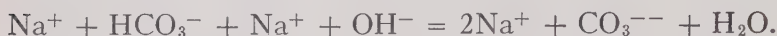


and



**56.** To change sodium acid carbonate,  $\text{NaHCO}_3$ , into sodium carbonate,  $\text{Na}_2\text{CO}_3$ , two methods are available.

The salt can be dissolved in water and treated with 1 equivalent of NaOH, when the  $\text{HCO}_3^-$  will be neutralized by the added  $\text{OH}^-$ , as shown by the equation

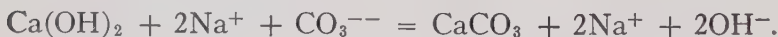


The resulting solution yields solid  $\text{Na}_2\text{CO}_3$  on evaporation. Again, the acid carbonate is capable of another kind of decomposition, represented by the equation,

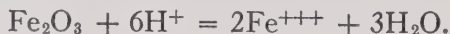


Since two of the substances produced by this reaction are volatile, the reaction can be made to proceed so as to produce them by heating the mixture in an open vessel so that they can escape.

**57.** To change  $\text{Na}_2\text{CO}_3$  to NaOH, it is necessary to remove the  $\text{CO}_3^{--}$  and supply  $\text{OH}^-$ . Since both sodium compounds are soluble, the insolubility of some other substances must be invoked. We need a hydroxide of some metal which is more soluble than the corresponding carbonate. The best one for this purpose is  $\text{Ca}(\text{OH})_2$ , which is itself scarcely soluble, especially in a solution of NaOH. The insolubility of  $\text{CaCO}_3$  causes the following reaction to take place, whereas any excess of  $\text{Ca}(\text{OH})_2$ , together with the  $\text{CaCO}_3$  produced, can be filtered off:



**58.** Iron rust can be dissolved by moderately dilute hydrochloric acid, as shown by the equation:



In dissolving a rust or ink stain off a delicate fabric it is not desirable, however, to use such concentrated acid. More dilute  $\text{H}^+$  can be used if the reaction is aided by the removal of one of the products. This is accomplished by using oxalic acid, which furnishes both dilute  $\text{H}^+$ , since it is a rather weak acid, and also oxalate ion,  $\text{C}_2\text{O}_4^{--}$ , which



unites with the free ferric ion to form a complex ion (see paragraph 21). The reaction is



### EXERCISES

1. Which of the following substances, when added to water, will give an acid reaction, which alkaline, and which neutral: (1) NaCl; (2)  $\text{CO}_2$ ; (3) NaAc; (4)  $\text{NaNO}_3$ ; (5) CaO; (6)  $\text{K}_2\text{CO}_3$ ; (7)  $(\text{NH}_4)_2\text{SO}_4$ ; (8) Ca; (9) sodium borate; (10)  $\text{BaCl}_2$ ?

2. Can you give a way for demonstrating the hydrolysis of  $\text{Al}_2(\text{SO}_4)_3$  without an indicator?

3. Write in order of decreasing acidities: 1  $M$ - $\text{H}_2\text{SO}_4$ ; 1  $M$ -HAc; 1  $M$ - $\text{NH}_4\text{Ac}$ ; 1  $M$ -NaAc; 1  $M$ - $\text{NH}_4\text{OH}$ ; 1  $M$ -HCl; 1  $M$ - $\text{NH}_4\text{Cl}$ ; 0.1  $M$ - $\text{Ba}(\text{OH})_2$ .

4. Arrange the following solutions in order of decreasing concentration of  $\text{OH}^-$ : (1) 0.5  $M$ -NaAc; (2) 0.1  $M$ - $\text{Na}_2\text{CO}_3$ ; (3) 0.1  $M$ - $\text{NH}_4\text{Cl}$ ; (4) 0.1  $M$ - $\text{NH}_4\text{Ac}$ ; (5) 0.1  $M$ -NaOH; (6) 0.1  $M$ - $\text{Ba}(\text{OH})_2$ ; (7) a solution made by dissolving 0.112 g. of CaO in 200 cc. of water.

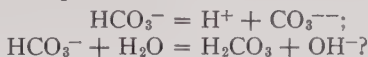
5. Why may it be necessary to use different indicators for titrating different acids and bases?

6. What indicator could you use to distinguish between (a) distilled water and 0.001  $M$ -NaOH; (b) 0.001  $M$ -NaOH and 0.1  $M$ -NaOH? State the distinguishing colors in each case.

7. Which of the two salts,  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ , would be more hydrolyzed when dissolved in water?

8. What is the effect on a water glass (sodium silicate) solution of (a) exposure to the  $\text{CO}_2$  in the air; (b) the addition of a solution of ammonium chloride?

9. (a) How can you determine by experiment which of the following reactions goes farther in pure water:



(b) What is the net result of both reactions?

10. Point out the relation between the strengths of bases and acids and the hydrolysis of the corresponding ions.

11. How would you prepare (a) pure solid  $\text{CuSO}_4$  from  $\text{CuCl}_2$ ; (b) pure solid  $\text{CuCl}_2$  from  $\text{CuSO}_4$ ; (c)  $\text{CaCO}_3$  from  $\text{CaSO}_4$ ; (d)  $\text{CaSO}_4$  from  $\text{CaCO}_3$ ; (e) solid NaCl from  $\text{NH}_4\text{Cl}$ ?

12. How could you determine by experiment whether  $\text{CaCO}_3$  or  $\text{CaSO}_4$  is more soluble in water?

13. Describe a simple experiment that would enable you to decide whether  $\text{CaC}_2\text{O}_4$  is more or less soluble than  $\text{CaCO}_3$ .

14. What substances would remain as solids and would be evolved as gases when solutions of the following are evaporated: (a)  $\text{Zn}^{++}$ ,  $\text{Cl}^-$  and excess of  $\text{H}^+$  and  $\text{SO}_4^{--}$ ; (b)  $\text{Zn}^{++}$ ,  $\text{Cl}^-$  and excess of  $\text{H}^+$  and  $\text{NO}_3^-$ ?

15. (a) Explain briefly why solid  $\text{BaCO}_3$  and solid  $\text{BaAc}_2$  are soluble in dilute  $\text{HCl}$  solution while solid  $\text{BaSO}_4$  is not. (b) Write equations.

16. What is the effect of (1)  $\text{NH}_4\text{Cl}$  solution, (2)  $\text{HNO}_3$  solution, (3)  $\text{H}_2\text{CO}_3$  solution, upon a precipitate of  $\text{Ca}(\text{OH})_2$ ? Explain in each case.

17. If, when 2 moles of  $\text{NaCl}$  and 1 mole of  $\text{H}_2\text{SO}_4$  are brought together, the reaction ceases when the  $\text{HCl}$  gas produced exerts a pressure of 10 atmospheres at  $77^\circ$  in a volume of 2 liters, (a) how many moles each of  $\text{NaCl}$  and  $\text{H}_2\text{SO}_4$  have reacted; (b) what fraction of each has reacted; (c) how might the quantities reacting be increased?

18. Write the formulas of the various molecules or ions present and state the approximate concentration of each when the following are put into 1 liter of water: (1) 0.02 mole of  $\text{CaCl}_2$ ; (2) 0.02 mole of  $\text{CaCl}_2$  and 0.03 mole of  $\text{NaCl}$ ; (3) 0.02 mole  $\text{CaCl}_2$  and 0.05 mole  $\text{Na}_2\text{CO}_3$ ; (4) 0.01 mole of  $\text{CuCl}_2$ ; (5) 0.02 mole  $\text{CaCl}_2$ , 0.02 mole  $\text{Na}_2\text{SO}_4$  and 0.02 mole  $\text{Na}_2\text{CO}_3$ ; (6) 1 mole  $\text{NH}_3$ ; (7) 1 mole  $\text{NH}_3$  and 0.5 mole  $\text{NaOH}$ ; (8) 1 mole  $\text{NH}_3$  and 1 mole  $\text{HCl}$ ; (9) 1 mole  $\text{NH}_4\text{OH}$ ; (10) 1 mole  $\text{NH}_3$ , 0.1 mole  $\text{AgNO}_3$  and 0.1 mole  $\text{NaCl}$ ; (11) 0.01 mole  $\text{AgNO}_3$ , 0.05 mole  $\text{KCl}$  and 0.05 mole  $\text{KI}$ .

19. How could you determine experimentally whether the  $\text{NH}_3$ , the  $\text{NH}_4^+$  or the  $\text{OH}^-$  of an ammonium hydroxide solution is responsible for the formation of a complex ion with a nickel ion?

20. The following can exist together in equilibrium at suitable concentrations:  $\text{Ag}_2\text{O} + \text{H}_2\text{O} + 4\text{NH}_3 = 2\text{Ag}(\text{NH}_3)_2^+ + 2\text{OH}^-$ . Explain how the equilibrium would be affected (1) by boiling, (2) by adding  $\text{NaOH}$ , (3) by adding  $\text{NH}_4\text{NO}_3$ , (4) by adding  $\text{Ag}_2\text{O}$ , (5) by adding  $\text{KNO}_3$ .

21. What would be present and approximately at what concentration when the following substances are mixed: (a) 0.1 mole  $\text{HgNO}_3$ , 0.1 mole  $\text{KOH}$ , 1 liter of water; (b) 0.1 mole  $\text{ZnSO}_4$ , 22.4 liters of  $\text{NH}_3$  gas at standard conditions, 1 liter of water; (c) 1 mole  $\text{BaCl}_2$ , 1 mole  $\text{CaCl}_2$ , 1 mole  $\text{H}_2\text{SO}_4$ , 10 liters of water; (d) 1 mole  $\text{Zn}$ , 0.5 mole  $\text{HgCl}_2$ , 500 cc. of water?

22. How would you prepare a pure silver compound and a pure copper compound from a mixture of solid silver chloride and cupric hydroxide? Write equations.

23. In the following list of ions:  $\text{H}^+$ ,  $\text{Ba}^{++}$ ,  $\text{Ag}^+$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{--}$ ,  $\text{Ac}^-$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{--}$ ,  $\text{CN}^-$ ,  $\text{OH}^-$ , state each pair that would tend to combine largely if brought together in dilute solution. In each case give reason for your answer and write equation.

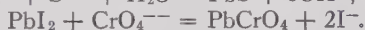
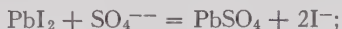
24. What is an amphoteric substance?

25. Can the following substances be present in moderate concentration in the same solution? If not, what is formed?  $\text{H}^+$  and  $\text{NO}_3^-$ ;  $\text{H}^+$  and  $\text{OH}^-$ ;  $\text{H}^+$  and  $\text{SO}_4^{--}$ ;  $\text{H}^+$  and  $\text{CO}_3^{--}$ ;  $\text{H}^+$  and  $\text{C}_2\text{O}_4^{--}$ ;  $\text{Ca}^{++}$  and  $\text{CO}_3^{--}$ ;

$\text{Ca}^{++}$  and  $\text{H}_2\text{CO}_3$ ;  $\text{OH}^-$  and  $\text{H}_2\text{CO}_3$ ;  $\text{H}_2\text{CO}_3$  and  $\text{CO}_3^{--}$ ;  $\text{HAc}$  and  $\text{CO}_3^{--}$ ;  $\text{Al}^{+++}$  and  $\text{OH}^-$ ;  $\text{Cu}^{++}$  and  $\text{NO}_3^-$ ;  $\text{Ag}^+$  and  $\text{NH}_3$ ;  $\text{Hg}^{++}$  and  $\text{Cl}^-$ .

26. Given the following reactions, arrange the compounds of copper involved so far as you can in a list according to increasing ability to hold  $\text{Cu}^{++}$ . (a)  $\text{H}_2\text{S}$  gives no precipitate in a cyanide solution of copper; (b) copper sulfide is insoluble in ammonia; (c) ferrocyanide ion added to copper ammonia complex solution precipitates copper ferrocyanide; (d) copper hydroxide is soluble in ammonia.

27. Given the following reactions, arrange the compounds of lead involved so far as you can in a list according to increasing ability to hold  $\text{Pb}^{++}$ .



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## Chapter XIV

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### *The Effect of Pressure and Temperature upon Equilibrium*

1. When chemical equilibrium has been reached it is possible, as we have seen in the two previous chapters, to bring about a further reaction by altering the concentration of one or more of the reacting substances, which causes that reaction to proceed which will tend to restore the original concentration, or, as we may say, to neutralize the effect of the change. It is likewise possible to affect equilibrium by changing the total pressure to which the system is subject, and by changing its temperature. We will now inquire into the direction in which a reaction must proceed in order to restore equilibrium when subjected to changes in pressure or temperature.

**2. Effect of Changing Total Pressure upon a System in Equilibrium.** If we have an equilibrium between a liquid and its vapor, as discussed in Chapter III, we have seen that an increase in the pressure tends to cause vapor to condense, since the number of gaseous molecules is thereby diminished, relieving the pressure. We have seen, also, that this is in harmony with the kinetic theory. Now, the same effect is always produced, no matter how complex the equilibrium. An increase in pressure always tends to produce the system having the smaller volume, a decrease in volume tending to relieve the increase in applied pressure. If, then, the applied pressure can be relieved by not only the contraction of the substances composing the system

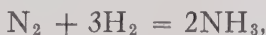
but by some reaction between them, as well, the increase of pressure will tend to shift equilibrium, if previously attained, so as to produce more of the substances having the smaller volume. The effect of pressure will, of course, be greater the greater the change in volume due to the reaction, and hence greatest in reactions involving changes in the number of gaseous molecules.

3. Suppose, for example, that we have a closed vessel containing  $\text{SO}_3$ ,  $\text{SO}_2$  and  $\text{O}_2$  in equilibrium, which has been reached by the substances reacting in one direction or the other, as represented by the equation,



We see from the equation that when  $\text{SO}_3$  is formed there is a change in the number of molecules in the proportion 3 to 2. If pressure is applied to the three gases in equilibrium, it will compress them, resulting in a decrease in volume. A further decrease is possible, however, by the union of some of the  $\text{SO}_2$  with some of the  $\text{O}_2$ , and the consequent diminution in the number of molecules, relieving somewhat the pressure applied. Starting, in two experiments, with identical amounts of  $\text{SO}_2$  and  $\text{O}_2$  at the same temperature, with a catalyst present, or else waiting for equilibrium to be established, we find that more  $\text{SO}_3$  will be produced when equilibrium is finally attained if the pressure is high than if it is low.

4. The same conclusion may be drawn with respect to the reaction,



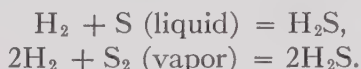
which shows that ammonia is formed with a diminution in the number of molecules. A high pressure would favor that reaction which would yield the smaller volume, thus relieving, as far as possible, the high pressure applied.

5. On the other hand, with the equilibria,



with no change in the number of gaseous molecules during a reaction, pressure will be without effect on the amounts formed.

6. In predicting the effect of pressure we must have regard to the physical states of the substances involved under the conditions of the experiment. It is possible, for instance, by using either liquid sulfur or sulfur vapor to make  $\text{H}_2\text{S}$  directly from its elements. The respective reactions may be represented by the equations,



In the first reaction there is practically no change in volume, if the reaction is done at constant pressure, as the volume of the liquid sulfur is negligible. Therefore, the relative amounts of  $\text{H}_2$  and  $\text{H}_2\text{S}$  present at equilibrium will be practically independent of the pressure applied, or of the volume of the vessel in which the reaction takes place. In the second process, where the conditions are such that the sulfur is in the vapor state, the formation of  $\text{H}_2\text{S}$  at constant pressure results in a decrease in volume, hence the higher the pressure the greater the amount of  $\text{H}_2\text{S}$  formed.

7. Not only is the effect on the direction indicated by the above discussion, but its magnitude also depends upon the magnitude of the volume change during the reaction. Thus a tenfold increase in total pressure will produce a much greater increase in the amount of  $\text{NH}_3$  produced from  $\text{N}_2$  and  $\text{H}_2$  than in the amount of  $\text{SO}_3$  produced from  $\text{SO}_2$  and  $\text{O}_2$ , since the decreases in volume in the two reactions are respectively from 4 to 2 and from 3 to 2. For the same reason very great changes in pressure have to be applied in order to have much effect on equilibria between liquids and solids only, where only small changes in volume occur.

**8. Effect on Equilibrium of Changing the Temperature.** In order to appreciate the effect of changing temperature upon a system in equilibrium, we must realize that the im-



mediate effect of any difference in temperature is to determine the flow of heat. If we have a tank of water at  $20^{\circ}\text{C.}$ , and put into it a piece of iron at a temperature of  $30^{\circ}$ , heat will flow from the iron to the water in the tank, tending to equalize the temperature. If, on the other hand, the piece of iron is at a temperature of  $10^{\circ}$ , when it is put into the water heat will flow from the water into the iron. Suppose, now, that we have a closed vessel containing  $\text{SO}_2$ ,  $\text{O}_2$  and  $\text{SO}_3$ , in equilibrium, in an oven at a temperature of  $500^{\circ}$ , and we remove it to another oven in which the temperature is  $550^{\circ}$ . Just as with the piece of iron in the former case, so here heat will flow into the vessel and its reacting mixture. The immediate effect of this heat will be to increase the temperature, the heat content, of the inclosed gases. There is, however, another way in which heat may be absorbed by the mixture, that is, by the reaction proceeding in the direction which absorbs heat. The direction of the reaction for heat absorption is shown by the complete thermochemical equation,



Since heat is evolved by the formation of  $\text{SO}_3$ , it will be absorbed by the reverse reaction, in which  $\text{SO}_3$  is dissociated into  $\text{SO}_2$  and  $\text{O}_2$ , hence the effect of bringing the reacting mixture to the higher temperature is to shift the equilibrium so as to form less  $\text{SO}_3$ .

9. If, on the contrary, the vessel with its equilibrium mixture is put into an oven at  $450^{\circ}$ , the heat will flow out of it. This heat will be furnished not only by the cooling of the contained gases, but also by their reacting to some extent to give off heat; accordingly, more  $\text{SO}_3$  is present at equilibrium at the lower temperature.

10. In the formation of  $\text{NO}$  from its elements heat is absorbed, as shown by the equation,



Consequently, if we have these gases in equilibrium, a rise in temperature will favor the absorption of heat in every possible way, which will not only cause the temperature of the gases to increase, but will also tend to form more NO. We see here that the higher the temperature the more NO will be obtained at equilibrium, while with  $\text{SO}_3$  the reverse is true, the higher the temperature the less  $\text{SO}_3$  is obtained at equilibrium.

11. Considerations of this sort apply to every sort of equilibrium and enable us either to predict the effect of changing the temperature from the sign (and magnitude) of the heat of reaction, or, conversely, to predict the latter from the former. As an illustration of this reverse process, let us consider a saturated salt solution where we find that the higher the temperature the more soluble is the salt, and ask ourselves whether this salt evolves or absorbs heat when more dissolves under equilibrium conditions. We have found by experiment that raising the temperature causes more salt to dissolve. From our theory we conclude that raising the temperature also favors any process that can take place with absorption of heat. Putting these two statements together we conclude that this salt absorbs heat on dissolving, since its solubility increases with the temperature. By similar reasoning, any salt that becomes less soluble as the temperature increases must have positive heat of solution, that is, it must evolve heat on dissolving.

12. **Simultaneous Consideration of All Factors Governing Reactions.** In Chapter XI we considered the velocity of chemical reactions, as it is affected by concentration, temperature and the presence of catalysts. We have also considered separately the effect of concentration, pressure and temperature upon chemical equilibrium and are now prepared to consider the simultaneous effect of these factors in controlling chemical reactions. We must again emphasize the fact that the question of velocity is quite distinct from

that of equilibrium. If we should put some calcium fluoride,  $\text{CaF}_2$ , and some calcium sulfide,  $\text{CaS}$ , into separate beakers of water, we might conclude from a hasty examination that both are very insoluble. As a matter of fact, the small amount of the solid going into solution is due to very different reasons in the two cases. Calcium fluoride is truly insoluble, and no amount of time or stirring would cause more than a very small amount of it to dissolve. On the other hand, calcium sulfide appears to be insoluble because, in order to dissolve, it must hydrolyze, giving  $\text{Ca}(\text{OH})_2$  and  $\text{Ca}(\text{SH})_2$ , a process which takes place very slowly. Again, calcium chromate,  $\text{CaCrO}_4$ , is more soluble in cold water than in hot, if sufficient time is allowed for the solution to become saturated, but it will dissolve much faster in hot water than in cold, so that after a given time more might be found in a hot than in a cold solution, although eventually the latter would contain more. It is thus very important, in attempting to realize difficult reactions, to remember that speed and equilibrium are two different considerations, and that conditions which favor the desired equilibrium may not favor its rapid attainment, and vice versa. A discussion of the complete conditions for realizing certain important reactions will make this clearer.

### 13. The "Contact Process" for Making Sulfuric Acid.

We have seen above that to make  $\text{SO}_3$  from  $\text{SO}_2$  and  $\text{O}_2$  a low temperature is desirable in order to give the most complete yield of  $\text{SO}_3$ . By recalling the discussion in Chapter XI, however, we will see that the lower the temperature the more slowly will the desired equilibrium be reached. We must therefore distinguish between the amount of  $\text{SO}_3$  which would be produced in infinite time and the amount that would be produced in a given time. This difference may be brought out by the curves in the accompanying figure, Fig. 1, where the heavy line indicates the per cent of the total possible amount of  $\text{SO}_3$  which would be obtained at equilibrium, provided that sufficient time were allowed.

This time necessary for reaching equilibrium grows enormously as the temperature is lowered, with the result that it is practically impossible to reach equilibrium except at high temperatures, where the amount of  $\text{SO}_2$  converted into  $\text{SO}_3$  is so small that it would not be profitable to use the reaction. The dotted lines indicate the actual approach to equilibrium in a given time, showing how, by allowing more time, more  $\text{SO}_3$  is obtained. At the higher tempera-

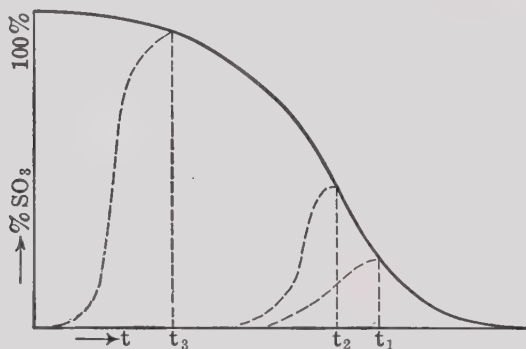


FIG. 1. Combined effect on yield of temperature and time.

tures, such as  $t_1$  and  $t_2$  in the figure, where the reaction occurs with measurable speed, no amount of waiting will give a satisfactory yield of  $\text{SO}_3$ . In order to work at temperatures at which the equilibrium is favorable, a new factor must be invoked to increase the velocity. This is attained in practice by the use of catalysts,  $\text{Fe}_2\text{O}_3$  and finely divided platinum. This allows the desired velocity to be attained at a much lower temperature,  $t_3$  in the figure, where the equilibrium is favorable to a good yield of  $\text{SO}_3$ . The contact of the gases with this solid catalyst gives the name "contact process." Sulfuric acid is made by dissolving the sulfur trioxide in water.

14. The speed of the reaction, and also the desired equilibrium, might be influenced in the right direction by having the reaction take place under high pressure. This involves

difficulties in the way of more complicated machinery that it is preferred to avoid in practice. Since the  $\text{SO}_2$  must be paid for, while the  $\text{O}_2$  is obtained free from the air, it is more important to use up the  $\text{SO}_2$  completely than the  $\text{O}_2$ . This is done by taking the air in considerable excess of the equivalent amount required. We may summarize in tabular form our conclusions concerning the best conditions for realizing this reaction.

	TO FAVOR LARGE AMOUNT OF $\text{SO}_3$ AT EQUILIBRIUM	TO FAVOR HIGH SPEED EITHER OF FORMATION OR DECOMPOSITION
Total pressure . . . . .	High	High
Temperature . . . . .	Low	High
Other factors . . . . .	Excess of $\text{O}_2$	Catalyst

To illustrate the conditions to be used in practice, there may be added a table showing the yield of  $\text{SO}_3$  that has been calculated, using a gas mixture at a total pressure of 1 atmosphere, with the following partial pressures:  $\text{SO}_2$ , 0.07 atm.;  $\text{O}_2$ , 0.10 atm.;  $\text{N}_2$ , 0.83 atm.

Temperature . . . . .	434°	550°	645°
Maximum yield, per cent $\text{SO}_3$ . .	99	85	60

**15. The Synthesis of Ammonia.** If we compare the reaction for the synthesis of ammonia,



with the above reaction for making  $\text{SO}_3$ , we see that the same conditions are indicated for realizing this reaction as for the former. This reaction, however, is exceedingly slow, so that even with the best catalyst that has been discovered after extensive search, iron, advantage must be taken of high pressure in aiding both the speed and the equilibrium at the temperatures at which the reaction will take place with measurable velocity.

The effect of both temperature and pressure on the yield of  $\text{NH}_3$  at equilibrium is indicated in the following figures:

TEMPERATURE	YIELD OF $\text{NH}_3$ , IN PER CENT	
	At 1 Atmosphere	At 100 Atmospheres
800° . . . . .	0.011	1.1
700° . . . . .	0.021	2.1
600° . . . . .	0.048	4.5
500° . . . . .	0.13	10.8

A further lowering of temperature below 500° to improve the yield would give too slow a reaction, so that the process is worked at about this temperature, and under pressures up to 200 atmospheres. As the  $\text{N}_2$  and  $\text{H}_2$  pass over the catalyst they unite partially to form  $\text{NH}_3$ . The gases are then passed through a cooling coil in which the  $\text{NH}_3$  is condensed to liquid and removed. The  $\text{N}_2$  and  $\text{H}_2$  again pass over the heated catalyst, again forming the equilibrium amount of  $\text{NH}_3$  and so on. The removal of  $\text{NH}_3$  is compensated by pumping in fresh  $\text{H}_2$  and  $\text{N}_2$ .

This process is now on a working basis and helping to solve the problem of making the inert nitrogen of the atmosphere available for our needs for fertilizer and explosives. It is of interest to note that it was not the discovery of the so-called "practical man," but was the result of extended and difficult scientific research along the lines here indicated. The conditions employed are such as would not occur to one not well versed in the theory, and call for pressures such as were never before used in a similar process, requiring the development of special alloys to withstand them.

**16. The Synthesis of Nitric Oxide.** We have already referred briefly to the reaction,



We see that the formation of  $\text{NO}$  would be aided by the following conditions, which we will tabulate as before.



	TO FAVOR LARGE AMOUNT OF NO AT EQUILIBRIUM	TO FAVOR HIGH SPEED EITHER OF FORMATION OR DECOMPOSITION
Total pressure . . . . .	No effect	High
Temperature . . . . .	High	High

As a consequence of these conclusions, we see that NO should be formed more rapidly and also more completely at high temperatures. That this is true is seen from the following figures on the basis of experiments:

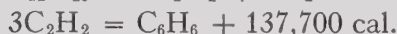
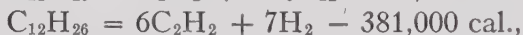
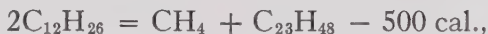
Temperature . . . . .	1540°	1920°	2930°	3930°
Per cent NO at equilibrium, starting with air . . . . .	0.37	0.97	5.0	10

Obviously NO is only stable, in a true sense, at extremely high temperatures, and both a favorable equilibrium and high speed in attaining it are aided by high temperatures such as those given by an electric arc. The problem is then to get it down to ordinary temperature without letting the equilibrium shift back to  $N_2$  and  $O_2$  as it cools. This is done by cooling it sufficiently rapidly as the gas mixture leaves the arc. There is also an electrical effect, due to the arc, tending to give a greater yield than is indicated by the above conditions of ordinary equilibrium.

At ordinary temperatures NO unites readily with more  $O_2$  to form  $N_2O_4$ , which will also dissolve in water, forming a mixture of nitric and nitrous acids. The  $N_2O_4$  may also be passed over slaked lime, giving a mixture of calcium nitrite and nitrate, which is used as fertilizer to supply nitrogen to the soil. This process was once used successfully on a commercial scale in Norway.

**17. The "Cracking" of Petroleum.** The principles above set forth have been of great aid in "cracking" the heavier molecules of petroleum so as to produce lighter molecules of more volatile substances, such as benzene,  $C_6H_6$ , toluene,  $C_6H_5CH_3$ , and those like  $C_5H_{12}$ ,  $C_6H_{14}$ ,  $C_7H_{16}$ , etc., which are contained in gasolene. It has been

found possible to control the nature of the products to a remarkable degree by designing apparatus that would permit of the independent control of temperature and pressure. The same substance is capable of a number of different transformations which would be influenced in different ways by changing the pressure and temperature. The probable effect of these factors may be predicted by the aid of the complete equations showing both the volume changes and the heats of reaction. The subject is too complicated for further discussion here, and we will merely give for illustration several equations showing possible reactions for  $C_{12}H_{26}$ , a prominent constituent of kerosene.

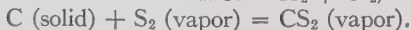


It is evident that the equilibria in these reactions would be influenced in very different ways by pressure and temperature.

### EXERCISES

1. If the volume of a solution is greater than that of the salt and water from which it is made, how will the solubility of the salt change when pressure is applied to the saturated solution?

2. In which direction would each of the following equilibria be displaced by decreasing the total pressure? (Explain.)



3. Ammonium chloride dissolves with considerable absorption of heat. How is its solubility affected by the temperature?

4. The solubility of sodium chloride increases very slightly with temperature. What can be concluded concerning its heat of solution?

5. When  $AgCl$  is prepared by mixing its ions heat is evolved. Is the precipitate more soluble in hot or in cold water? (Explain.)

6. Explain how temperature would affect the production of  $H_2S$  according to the reaction:  $H_2 + S = H_2S + \text{heat}$ .

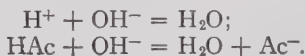
7. The formation of benzene from acetylene according to the reaction  $3\text{C}_2\text{H}_2 = \text{C}_6\text{H}_6 + 137,700 \text{ cal.}$  takes place slowly at a high temperature (benzene being a vapor) and is reversible.

(a) What weight of benzene could be made by the complete conversion of 49.3 liters of acetylene, measured at  $27^\circ \text{C.}$  and 1 atmosphere? *Ans.* 52 g.

(b) State and explain the experimental conditions you would adopt to secure the maximum yield of benzene from acetylene in a given time.

8. Knowing that the neutralization of strong acids by strong bases evolves much heat, it is possible to decide how the ionization of water varies with the temperature. Trace the connection.

9. Acetic acid is more highly ionized at higher than at lower temperatures. Which of the following reactions, consequently, will evolve more heat?



# Chapter XV

## *Oxidation and Reduction*

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1. In the previous chapters our attention has been largely confined to reactions in which there are no changes in oxidation number. In Chapter IX, however, brief mention was made of reactions in which such changes do occur, and it was there pointed out that oxidation consists essentially of an increase in oxidation number, or loss of electrons, and reduction of a decrease in oxidation number or gain of electrons. We are now prepared to give fuller attention to such reactions, considering, first, the writing of equations representing them, and, second, the oxidizing and reducing powers of the substances involved.

2. Whenever an element is oxidized some element must be reduced. The substance containing the element which is oxidized is called the **reducing agent**, since it is responsible for the reduction of the other element. Conversely, the substance which causes an increase in valence is the **oxidizing agent**, and contains an element which is reduced. The following table illustrates these terms:



Oxidation

Number	0	6	2, 6	4
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Element oxidized, Cu.	Oxidizing agent, $\text{H}_2\text{SO}_4$ .
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Element reduced, S.	Reducing agent, Cu.
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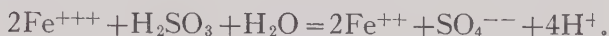
Oxidation

Number	1, -2	0	0	-1
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Element oxidized, S.

Oxidizing agent,  $\text{I}_2$ .

Element reduced, I.

Reducing agent,  $\text{H}_2\text{S}$ .

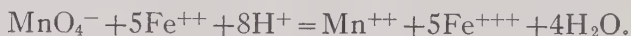
Oxidation

Number	3	4	2	6
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Element oxidized, S.

Oxidizing agent,  $\text{Fe}^{+++}$ .

Element reduced, Fe.

Reducing agent,  $\text{H}_2\text{SO}_3$ .

Oxidation

Number	7	2	2	3
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Element oxidized, Fe.

Oxidizing agent,  $\text{MnO}_4^-$ .

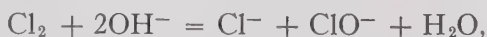
Element reduced, Mn.

Reducing agent,  $\text{Fe}^{++}$ .

**3. Writing Equations for Reactions Involving Oxidation and Reduction. The Substance Produced.** Before an equation can be written for any reaction it is necessary to know what substances are produced. This may be determined by experiment or predicted, in most cases, from a knowledge of the reacting substances. For example, when hot concentrated sulfuric acid reacts with copper it is possible to detect the evolution of sulfur dioxide by its odor, and the production of copper sulfate by the blue color it gives on the addition of water. When sulfurous acid acts upon ferric ion, the ferrous ion produced shows its presence by its faint green color, or by other characteristic tests, and the formation of sulfate ion can be proved by adding barium ion. One sufficiently familiar with the chemistry of iron and of sulfur would not need these tests, for he knows that when ferric ion decreases in oxidation number in acid solution it usually becomes ferrous ion, and that the corresponding

increase of oxidation numbers on the part of sulfurous acid would give sulfate ion. It is therefore important to know the oxidation numbers the elements are capable of assuming and the compounds characteristic of each valence.

4. For example, many of the metals, including the alkali and alkaline earth metals, silver, zinc, cadmium and aluminum, exhibit only one oxidation state in addition to that of the free metal, which is zero. Therefore a substance like aluminum ion,  $\text{Al}^{+++}$ , cannot be oxidized farther, nor can it be reduced to metal in water solution. Hence we would not expect it to take part in any oxidation or reduction process in aqueous solution. Chlorine shows the following oxidation states,  $-1, 0, +1, +3, +5, +7$ , which correspond to the compounds tabulated on page 129. Consequently, we would never find the chlorine in chloride ion,  $\text{Cl}^-$ , acting as an oxidizing agent, because it is already as completely reduced as it is capable of being. Likewise, if chlorine,  $\text{Cl}_2$ , acts as an oxidizing agent it must be reduced, and the only possible product would be chloride ion or one of its compounds. Again, knowing that chlorine reacts with hydroxide ion as follows:



we know that when  $\text{ClO}^-$  acts as an oxidizing agent in alkaline solution, the chlorine could not be reduced to the next lower valence, zero, corresponding to  $\text{Cl}_2$ , but would be reduced all the way to chloride ion.

5. The following table represents the substances characteristic of chromium in the valences of three and six respectively, and in acid, neutral or alkaline solution:

OXIDATION NUMBER	ACID	NEUTRAL	ALKALINE
3 . . .	$\text{Cr}^{+++}$	$\text{Cr}(\text{OH})_3$	$\text{CrO}_2^-$
6 . . .	$\text{Cr}_2\text{O}_7^{--}$	$\text{CrO}_4^{--}$	$\text{CrO}_4^{--}$



In accordance with the knowledge thus summarized, we would expect  $\text{Cr}^{+++}$  to be produced when a reducing agent acts upon  $\text{Cr}_2\text{O}_7^{--}$ . Similar information should be remembered for the other common elements giving compounds in which they show more than one valence.

**6. The Assignment of Oxidation Numbers to the Elements Oxidized and Reduced.** Having decided upon the substances produced by the reaction, the first step is to write their formulas, together with those of the substances reacting, upon the appropriate side of the equation, and to assign an oxidation number to the elements oxidized and reduced, as explained in Chapter V.

**7.** Let us illustrate the process by balancing the equation for the oxidation of  $\text{Fe}^{++}$  by  $\text{MnO}_4^-$ . The following scheme thus gives the various steps involved:

(a) Substances oxidized and reduced



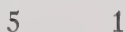
(b) Oxidation numbers



(c) Changes per atom



(d) Atoms required



(e) Molecules required



(f) Other molecules added to balance



Step (c), the change in oxidation number per atom, is got by noting that the iron changes from 2 to 3, while the manganese changes downward, from 7 to 2. To balance the reduction of 1 atom of manganese thus requires 5 atoms of iron, as shown in step (e). The oxidation and reduction are now balanced, and the coefficients assigned must not be disturbed in the final balancing of the other elements and

charges. To do this one may consider, first, either the discrepancy in oxygen atoms, or the discrepancy in charges. It will usually be found somewhat simpler to begin with the latter. In step (e) we have on the left  $+10 - 1$  or  $+9$ , and on the right  $+15 + 2$  or  $+17$ . We must, therefore, either add  $8\text{H}^+$  on the left or  $8\text{OH}^-$  on the right. Since the metallic ions given in the equation could not exist as such in an alkaline solution the solution is acidic, and we should add  $8\text{H}^+$  on the left. It will then be found that these 8 hydrogen atoms and the 4 oxygen atoms of the  $\text{MnO}_4^-$  will be balanced by adding finally  $4\text{H}_2\text{O}$  on the right, giving step (f) as the completed equation.

8. Let us next consider a reaction occurring in alkaline solution. We will indicate the steps used in balancing it just as in the preceding example.

(a) Substances oxidized and reduced



(b) Oxidation numbers

	3	1	6	- 1
--	---	---	---	-----

(c) Changes per atom	3	- 2		
----------------------	---	-----	--	--

(d) Atoms required	2	3		
--------------------	---	---	--	--

(e) Molecules required



(f) To balance charges, add  $2\text{OH}^-$  on left, and to balance oxygen and hydrogen,  $\text{H}_2\text{O}$  on right, getting:



9. There is sometimes confusion due to the presence in the same molecule of more than 1 atom of an element oxidized or reduced. As an example we will consider the oxidation of  $\text{SO}_2$  to  $\text{SO}_4^{--}$  by  $\text{Cr}_2\text{O}_7^{--}$  (in acid solution, since  $\text{Cr}_2\text{O}_7^{--}$  exists only in acid solution). Using the same steps as before, we have,

(a) Substances oxidized and reduced



(b) Oxidation numbers (of 1 atom)

4                  6                  3                  6

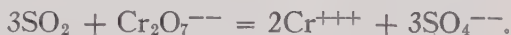
(c) Changes per atom

2                  - 3

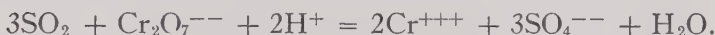
(d) Atoms required

3                  2

(e) Molecules required



(f) To balance charges add  $2\text{H}^+$  on left, and to balance H and O add  $\text{H}_2\text{O}$  on right, getting



The point to notice is that the required 2 atoms of Cr are already taken in the molecule of  $\text{Cr}_2\text{O}_7^{--}$ , whereas the coefficient 2 is required before the  $\text{Cr}^{+++}$  on the right.

10. We will take next a reaction in which the same element is both oxidized and reduced, viz., the reaction of active phosphorus with concentrated NaOH solution to form phosphine,  $\text{PH}_3$ , and hypophosphite ion,  $\text{H}_2\text{PO}_2^-$ .

(a) Substances oxidized and reduced



(b) Oxidation numbers                  0                  + 1                  - 3

(c) Changes per atom                                  1                  - 3

(d) Atoms required                                  4                  3                  1

(e) Molecules required                                   $\text{P}_4 = 3\text{H}_2\text{PO}_2^- + \text{PH}_3.$

(f) To balance charges add  $3\text{OH}^-$  on left, and to balance H and O add  $3\text{H}_2\text{O}$  on left, getting



11. Equations involving peroxides are sometimes troublesome, and we will therefore include one illustration.

(a) Substances oxidized and reduced

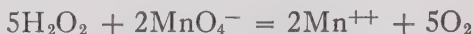


(b) Oxidation numbers      - 1      7      2      0

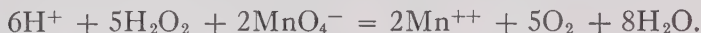
(c) Changes per atom      1    - 5

(d) Atoms required      5      1

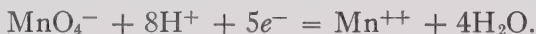
(e) Molecules required



(f) To balance charges, add  $6\text{H}^+$  on left, etc., getting



**12. An Alternative Method.** Since an element is oxidized when it gives up electrons and reduced when it takes on electrons, the number of electrons transferred may be made the basis for balancing an equation. For example, whenever  $\text{MnO}_4^-$  is reduced in acid solution it becomes  $\text{Mn}^{++}$ . To take care of the oxygen atoms in the  $\text{MnO}_4^-$  there will obviously be required  $8\text{H}^+$ , giving  $4\text{H}_2\text{O}$  and to balance the charges will require 5 electrons, giving for the oxidizing half of the reaction the half-equation,



The same result is achieved by writing in first the 5 electrons necessary to change the manganese from oxidation number 7 to oxidation number 2, and then adding the  $8\text{H}^+$  to produce  $4\text{H}_2\text{O}$ . If the substance oxidized is  $\text{Fe}^{++}$ , the reducing half of the reaction is  $\text{Fe}^{++} = \text{Fe}^{+++} + e^-$ . Obviously the former process can take the electrons from 5 times the latter, so that multiplying the latter half-equation by 5 and adding to the former gives



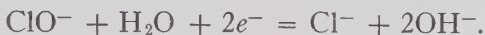
the same result as was previously obtained by the other method.

13. Let us give an illustration of the balancing of a reaction in alkaline solution by this method. To oxidize  $\text{CrO}_2^-$  to  $\text{CrO}_4^{--}$  requires  $4\text{OH}^-$ , giving

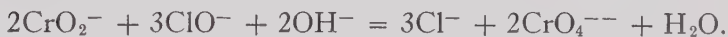


the 3 electrons being obviously necessary to make the equation balance.

To reduce  $\text{ClO}^-$  to  $\text{Cl}^-$  requires  $\text{H}_2\text{O}$ , giving  $2\text{OH}^-$ , so that



Multiplying this half-reaction by 3 and the former by 2 and adding cancels out the electrons, giving



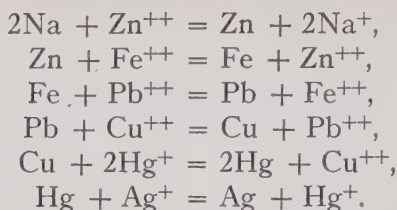
14. Although these methods may appear to be superficially different they rest upon the same theoretical foundation and will give identical results. The choice between them is largely a matter of taste, except that the half-reactions are those occurring at the electrodes in electrolysis and in electric batteries, so that they become very useful in electro-chemistry.

There is a theoretical advantage in the half-reaction method due to the fact that it avoids the arbitrary fixing of oxidation numbers, or assignment of shared electrons to one atom or another. The oxidation of  $\text{S}_2\text{O}_3$  to  $\text{SO}_4^{--}$ , for example, can be simply written



without deciding whether the oxidation numbers of the two sulfur atoms are  $-2$  and  $+6$  or  $0$  and  $+4$  or both  $+2$ .

**15. The Relative Oxidizing and Reducing Powers of Various Substances. The Metals and Their Ions.** It was pointed out in Chapter V that an element having a smaller affinity for its electrons can replace one having less positive ones in its compounds. This is illustrated by the following reactions, all of which take place quite readily:



In each of these cases the baser metal is oxidized by the ion of the nobler one, and it is evident that zinc will reduce not only ferrous ion, but lead, copper and silver ions as well. Likewise, silver ion can act as an oxidizing agent, not only to copper, but to all of the other metals represented. In all cases the metals act as the reducing agents, their reducing power decreasing as we descend the list, while the ions act as oxidizing agents, their oxidizing power increasing as we descend the list. This behavior may be summarized in Table 1.

TABLE 1

Oxidation ↑	Weak		Oxidizing Agents					Strong		Reduction ↓
	Na <sup>+</sup>	Zn <sup>++</sup>	Fe <sup>++</sup>	Pb <sup>++</sup>	Cu <sup>++</sup>	Hg <sup>+</sup>	Ag <sup>+</sup>			
	Na	Zn	Fe	Pb	Cu	Hg	Ag			
	Strong		Reducing Agents					Weak		

This table has been arranged so that any ion will be reduced if brought in contact with a metal to the left in the table. In order, however, for this arrangement to hold, the ions must all be in approximately equal concentration. If this is not the case, the positions of some may be reversed. Thus Hg<sup>+</sup> and Ag<sup>+</sup> have about the same oxidizing power, hence the reaction,



is easily reversible by changing the relative concentrations. The principles of equilibrium set forth in Chapter XII apply here also, so that a high concentration of Hg<sup>+</sup> and a low concentration of Ag<sup>+</sup> favor the reaction as read from left to right, whereas the reverse reaction is favored by reversing



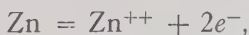
the relative concentrations. With most pairs of metals the corresponding reversal requires greater differences in concentration.

16. Many interesting applications of this oxidation-reduction series are possible. For example, it is evident that if a piece of zinc is put into a solution of ferrous ion there is a tendency for the latter to be reduced. Accordingly, if zinc and iron are in contact in an oxidizing solution, the former will be dissolved before the latter. This is the reason for the protective action of the zinc coating on "galvanized" iron.

17. When a piece of zinc is dropped into a solution of one of the ions to the right of it in the table, a reaction takes place such as the following:



Now this may be regarded as a transfer of positive electricity from the copper ion to the zinc, or, better, as the transfer of negative electrons from the zinc to the copper ion. If this transfer of electricity can be made to take place through a wire we will have an electric current, and the reaction can be made to do work. To do this the zinc must not be put directly into the solution of copper ion, but electrodes of the two metals must dip into solutions of their own ions, the solutions being separated by a porous partition or by the aid of their difference in density, as in the case in the well-known "gravity cell" illustrated in Fig. 1. At the zinc electrode the following process tends to take place:



while at the copper electrode the reaction is



Each of these processes can continue only if the stream of negative electrons, or atoms of electricity, can flow from the zinc to the copper, while the positive and negative ions

in the solution migrate towards their respective poles. For every mole of zinc that dissolves one mole of copper will be deposited and two faradays of electricity (see page 106)

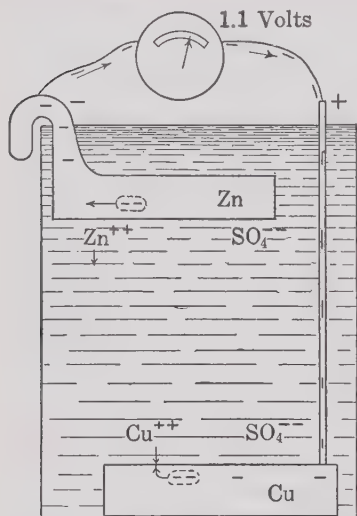


FIG. 1. Electric battery utilizing the reaction,  
 $\text{Zn} + \text{Cu}^{++} = \text{Cu} + \text{Zn}^{++}$ .

will travel through the wire. The electromotive force between the electrodes depends upon the difference between the tendencies of the metals to become ions, and also upon the relative concentration of the ions in the solution. If the concentration of zinc ion is diminished, or that of copper ion is increased, the reaction,



will have a greater tendency to take place, and will give a larger electromotive force when occurring in an electric battery. If silver ion and

silver are substituted for copper ion and copper, we will have a stronger oxidizing agent, a greater tendency to take up the electrons given off by the zinc and a battery of higher electromotive force.

18. The quantitative effect of changing concentration is given approximately by the formula  $\Delta E = \frac{0.059}{n} \log_{10} \frac{C_1}{C_2}$ , where  $\Delta E$  is the change in e.m.f. produced by changing the concentration of the ion from  $C_1$  to  $C_2$ . The charge of the ion is  $n$ . A cell made by having 2 zinc electrodes dipping respectively into 0.01 and 0.001 molal  $\text{Zn}^{++}$  solutions would have an e.m.f. of  $\Delta E = \frac{0.059}{2} \log \frac{0.01}{0.001} = 0.0295$  volts. The cell discussed in the preceding paragraph has an e.m.f. of 1.107 volts for molal concentrations of  $\text{Zn}^{++}$  and  $\text{Cu}^{++}$ . Changing the concentration of  $\text{Zn}^{++}$  to 0.001 molal would increase this e.m.f. to

$$1.107 + \frac{0.059}{2} \log \frac{1}{0.001} = 1.107 + 0.040 = 1.147 \text{ volts.}$$

19. The hydrogen electrode can be used to measure the hydrogen ion concentration of a solution. This consists of a small plate of platinum, made rough by depositing fine "platinum black" by electrolysis, and dipping partly into the solution and projecting above into an atmosphere of hydrogen. The gas dissolves sufficiently in the platinum to be capable of the reaction,  $\frac{1}{2}\text{H}_2 = \text{H}^+ + e^-$ , and set up a definite e.m.f. If two such electrodes were used, one dipping into 1  $M\text{-H}^+$ , the other into  $\text{H}^+$  of unknown concentration, the e.m.f. between the two electrodes could be used

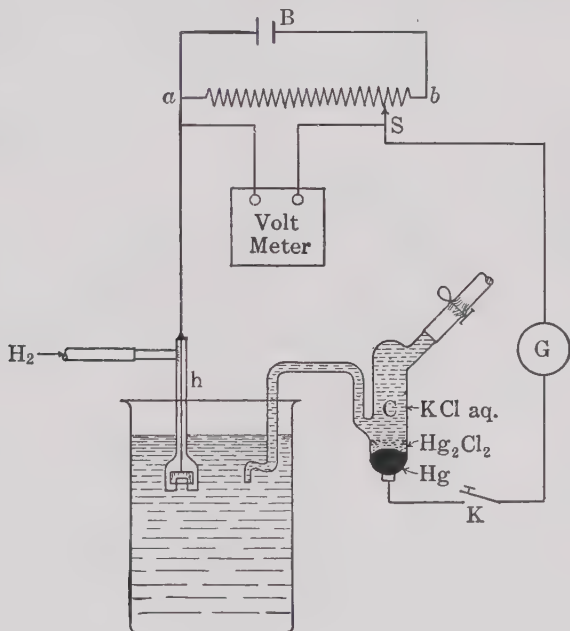


FIG. 2. Hydrogen electrode apparatus.

to calculate  $C_2$  in the above formula. It is more convenient, actually, to use a standard calomel electrode, mercury, covered with  $\text{Hg}_2\text{Cl}_2$  in 1  $M\text{-KCl}$ , in place of the known hydrogen electrode, since we already know the relation between these two. The apparatus is illustrated in Fig. 2. Figure 3 shows several curve types resulting from following the hydrogen ion concentration, plotted as pH (cf. Chapter XIII, Table 2) against equivalents of alkali added. Such curves throw much light on the processes taking place.  $\text{HCl}$ , being a strong acid, keeps the solution at high acidity as long as any of it is present. The concentration of  $\text{H}$  ion drops only one power of ten when the acid is nine-tenths neutralized, two powers of ten when it is 0.99 neu-

tralized, etc. There is a sudden rise in pH through the neutral point to strong alkalinity. Acetic acid is a moderately weak acid and hence the curve begins for a 0.1 molal solution at H ion concentration of 0.0013. As neutralization proceeds the accumulating acetate ion causes a rapid decrease in acidity, the H ion concentration becoming  $1.8 \times 10^{-5}$  when it is half neutralized, that is  $(\text{Ac}^-) = (\text{HAc})$ . The steep portion of the curve extends through a much smaller range than was the case for hydrochloric acid. This illustrates clearly why there is a much narrower choice

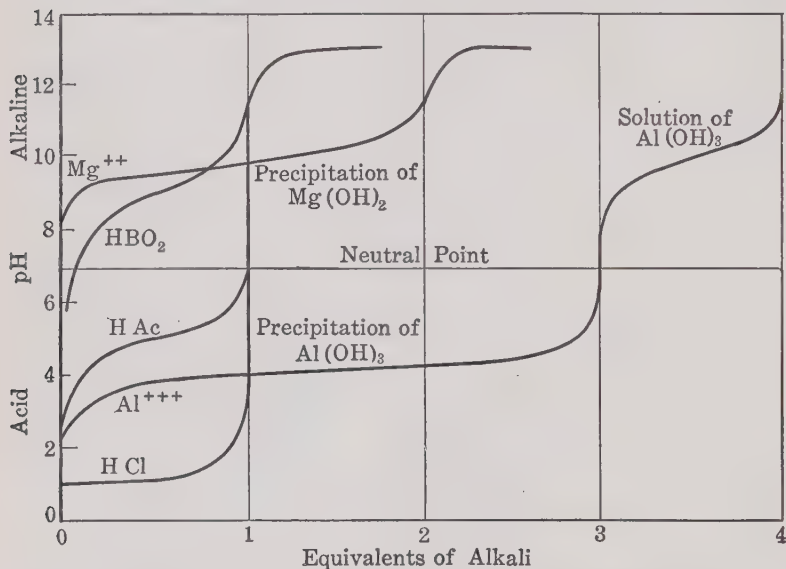


FIG. 3. Neutralization as followed by the aid of a hydrogen electrode.

of indicators for this titration than for the other and that the best results would be obtained for an indicator changing in the neighborhood of  $\text{pH} = 9$ . Boric acid is a very weak acid and can be neutralized only in a rather alkaline solution. Furthermore, the steepness of the curve at the end of the titration is not very great and even though an indicator were carefully chosen the color change could not be sharp. The precipitation of  $\text{Mg}(\text{OH})_2$  from  $\text{Mg}^{++}$  requires a rather alkaline solution and is practically complete on addition of two equivalents of alkali. To precipitate  $\text{Al}(\text{OH})_3$ , of course, requires three equivalents of alkali, but on account of the great insolubility of this substance it takes place in acid solution. The beginning of the curve shows an acidity due to the hydrolysis of  $\text{Al}^{+++}$ . Aluminum hydroxide dissolves in approximately one equivalent of alkali

showing that it acts as a mono-basic acid and that the principal ion present in the solution is  $\text{AlO}_2^-$  or  $\text{H}_2\text{AlO}_3^-$ .

20. The electromotive force of such a battery is thus a measure of the tendency of the reaction to take place, or the **chemical affinity** of the reaction, a term much used in the development of chemistry, but also much abused, for it has often been used very loosely. It is only in comparatively recent years that it has been given an exact definition. On this account it is desirable to substitute the term **free energy** for affinity. The electromotive force of the copper-zinc cell when normal solutions of copper and zinc sulfates are used is about 1.09 volts. The free energy of the reaction at these concentrations is the work it can do, which would be  $1.09 \times 2 \times 96,540$  volt-coulombs, or joules, per mole of reacting substances.

Table 2 illustrates the degree of correspondence between free energies,  $\Delta F$ , and heats of reaction,  $\Delta H$ .

TABLE 2

REACTION	$\Delta H$	$\Delta F$
$\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2 (\text{g}) = \text{H}^+ + \text{Cl}^-$	- 39,940	- 31,370
$\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$	- 13,330	- 19,120
$\text{Zn} + 2\text{H}^+ = \text{Zn}^{++} + \text{H}_2$	- 36,720	- 34,980
$\text{Ca}^{++} + \text{CO}_3^{--} = \text{CaCO}_3$	+ 2,780	- 10,920
$\text{Pb} + \text{Cl}_2 (\text{g}) = \text{PbCl}_2$	- 85,390	- 75,050
$\text{Fe}^{+++} + \text{Ag} = \text{Ag}^+ + \text{Fe}^{++}$	+ 14,300	+ 1,220

21. The reaction between zinc and silver ion may be utilized in cleaning the tarnish from silverware. The tarnish consists of silver sulfide,  $\text{Ag}_2\text{S}$ , and though this gives but a small concentration of silver ion, the free energy of the reaction is still sufficient for it to take place quite readily. If, therefore, a piece of zinc (aluminum will also serve) is placed in electrical contact with a piece of tarnished silver, both dipping into water containing a little salt to render it conducting, and hot to increase the speed of reaction, the following reaction takes place over the surface of the silver:



the electrons being furnished by the zinc. The sulfide ion liberated would, of course, undergo hydrolysis. The silver is thus restored instead of being rubbed off as in ordinary polishing.

**22.** If a solution containing the ions of two metals is electrolyzed, it is possible to reduce at the cathode, first the ion of the nobler metal, and afterwards that of the baser metal, by proper regulation of the electromotive force. It is possible thus to make an **electrolytic separation** of different metals, which is to be preferred, in many cases, to the ordinary methods of separation based upon the precipitation of insoluble compounds.

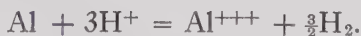
**23. The Solubility of Metals in Water, Acids and Alkalis.** When a metal dissolves in water, in alkali, or in dilute acids the substance reduced is usually hydrogen ion. Accordingly, it is desirable to introduce  $H^+$  and  $H_2$  into the table previously given. In attempting to do this we find an apparent discrepancy in the reactions of the metals with hydrogen ion, for iron will dissolve in dilute hydrogen ion, whereas zinc, if very pure, and especially if wet with mercury, will not. We find, however, that this is due to the difficulty which hydrogen has in depositing on a surface of pure zinc or mercury, for if a piece of platinum is dipped into the acid and brought into contact with the zinc, we find that the latter dissolves quite readily. The hydrogen is then deposited on the platinum, the electrons left behind when zinc is converted to zinc ion traveling through the metals to the platinum, where they neutralize the hydrogen ions, changing them into hydrogen gas. If we test the solubility of the various metals in dilute acids in this way, we find that all those to the left of copper in the table will dissolve, although lead and zinc will do so only with great difficulty, when pure, and in the absence of some more favorable surface for the hydrogen to deposit upon. The same difficulty is encountered in reducing hydrogen ion at certain cathodes, for a higher electromotive force is required to deposit hydrogen at a given rate on some surfaces than on others. A successively higher electromotive force is required with cathodes of the following substances: Pt (rough), Pt (smooth), Ag, Cu, Sn, Pb, Zn, Hg. Hydrogen



thus takes the place given in the more extended table on page 230, provided that a rough platinum surface is in electrical contact with the metal dissolving. We see, then, that copper, silver, mercury and the other noble metals will not dissolve in acids like dilute hydrochloric and sulfuric under any circumstances, while lead and the baser metals will dissolve in dilute hydrogen ion, provided that platinum is in contact with the metal, but that lead and zinc, or other base metals if amalgamated with mercury, may dissolve very slowly, or practically not at all. When impure zinc is used, the particles of foreign substances, like iron and carbon, furnish nuclei upon which the hydrogen can deposit with more ease; hence such zinc will dissolve at a reasonable rate.

24. As we approach the left side of the table, where the metals become baser, and better reducing agents, the hydrogen ion does not need to be so concentrated in order to act upon the metal, and even the extremely dilute hydrogen ion of water is able to oxidize and dissolve metals like calcium and sodium.

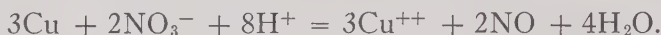
Aluminum dissolves easily in dilute hydrogen ion, the reaction being



If hydroxide ion is used instead of hydrogen ion, although the decrease in the concentration of the latter would tend, by itself, to stop the solution of the aluminum, at the same time the concentration of aluminum ion is decreased very greatly on account of the formation of the aluminate ion, a fact which aids the reaction, and compensates for the reduction in the hydrogen ion concentration. Hence aluminum will dissolve in alkali as well as in acid. The same is true of zinc.

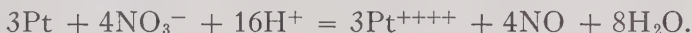
25. For the metals to the right of hydrogen in the table a stronger oxidizing agent than hydrogen ion is necessary. This is found, for some, in nitric acid, whose oxidizing action

is due to the reduction of nitrogen rather than of hydrogen. Copper, silver and mercury can accordingly be dissolved in nitric acid. A typical reaction is the following:



Sulfuric acid, if hot and concentrated, can oxidize copper, silver and mercury, its sulfur being reduced to  $\text{SO}_2$ .

**26.** When we come to the noblest metals, like gold and platinum, even the oxidizing power of nitric acid becomes insufficient. Instead, however, of seeking a stronger oxidizing agent, another principle is invoked. The following reaction will not take place with nitric acid alone:



Platinic ion, however, is prone to form a complex acid with hydrochloric acid,  $\text{H}_2\text{PtCl}_6$ , chlor-platinic acid (see page 175), and hence, if a mixture of hydrochloric and nitric acids, known as "aqua regia," is used instead of the nitric acid alone, the platinic ion, one of the products of the oxidation, is used up sufficiently to enable the reaction to proceed. This action of aqua regia is not due, as is often erroneously stated, to the fact that the chlorine liberated by the aqua regia ( $4\text{H}^+ + \text{NO}_3^- + 3\text{Cl}^- = \text{Cl}_2 + \text{NOCl} + 2\text{H}_2\text{O}$ ) is a stronger oxidizing agent than the nitric acid, for if this were the case chloride ion would not be oxidized by nitric acid. Chlorine is, however, a more rapid oxidizing agent, and the effectiveness of the aqua regia is doubtless due to this fact as well as to the formation of the complex chlor-platinic acid. The action of aqua regia on gold is quite analogous to that on platinum. In this case the complex chlor-auroic acid,  $\text{HAuCl}_4$ , is formed.

**27.** Cyanide ion,  $\text{CN}^-$ , forms such a firm complex with both aurous and auric ions that when it is present the oxygen of the air is sufficient to oxidize gold; the reaction is



This reaction is used in the "cyanide process" for the extraction of gold from its ores.

### 28. General Table of Oxidizing and Reducing Agents.

We may consider the oxidizing and reducing powers involved in changes other than those between the metals and their ions just considered. We find, for example, that chlorine will liberate bromine from bromide ion, and that bromine will liberate iodine from iodide ion. Accordingly, we may conclude that chlorine will liberate iodine from iodine ion. This information may be tabulated in the manner used previously for the metals, as follows:

Weak	Oxidizing Agents	Strong
$I_2$	$Br_2$	$Cl_2$
$I^-$	$Br^-$	$Cl^-$
Strong	Reducing Agents	Weak

By the aid of appropriate experiments we may find the place of other common substances in such a table, and also combine it with the table previously given. The following table gives an illustration of such arrangement.

29. It should be borne in mind that such an arrangement is not altogether rigid, but that it is affected by the concentrations of the reacting substances. According to the table, for example, one might infer that the following reaction would occur:



This would undoubtedly take place if  $Ag^+$  and  $I^-$  could act upon each other at ordinary concentrations without precipitating insoluble  $AgI$ . The same applies to the action of  $H_2S$  on  $Ag^+$ .

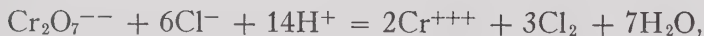
30. The hydrogen ion concentration affects the equilibrium in many cases. For example, the reaction



TABLE 3  
OXIDIZING AND REDUCING POWERS OF VARIOUS SUBSTANCES<sup>1</sup>

		Oxidation, electrons lost			
		→			
Strong	Zn		Zn <sup>++</sup>		Weak
	Fe		Fe <sup>++</sup>		
	Sn		Sn <sup>++</sup>		
	Pb		Pb <sup>++</sup>		
	H <sub>2</sub> on Pt		H <sup>+</sup>		
Reducing Agents	Sn <sup>++</sup>		Sn <sup>++++</sup>		Oxidizing Agents
	SO <sub>2</sub>		SO <sub>4</sub> <sup>--</sup> + H <sup>+</sup>		
	H <sub>2</sub> S		S		
	I <sup>-</sup>		I <sub>2</sub>		
	Fe <sup>++</sup>		Fe <sup>+++</sup>		
	Ag		Ag <sup>+</sup>		
	Br <sup>-</sup>		Br <sub>2</sub>		
	I <sub>2</sub>		IO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>		
	SO <sub>2</sub>		H <sub>2</sub> SO <sub>4</sub> , hot, concentrated		
	Cl <sup>-</sup>		Cl <sub>2</sub>		
Weak	NO		NO <sub>3</sub> <sup>-</sup> + conc. H <sup>+</sup>		Strong
	Cr <sup>+++</sup>		Cr <sub>2</sub> O <sub>7</sub> <sup>--</sup> + conc. H <sup>+</sup>		
	Mn <sup>++</sup>		MnO <sub>4</sub> <sup>-</sup> + H <sup>+</sup>		
	Pb <sup>++</sup>		PbO <sub>2</sub> + conc. H <sup>+</sup>		
		Reduction, electrons gained			
		←			

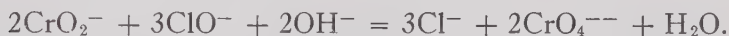
proceeds readily in dilute solution. It will be seen, however, that by diminishing the amount of water present and increasing the relative amount of acid the equilibrium is shifted in favor of those substances on the left, and, as a matter of fact, concentrated sulfuric acid readily liberates iodine from solid iodides. Similarly, the following reaction accords with the positions in the table of the substances involved:



and in concentrated acid the reaction proceeds in this way. The large amount of H<sup>+</sup> used up, however, indicates that

<sup>1</sup> This table has been expanded into an extensive table of Standard Oxidation-Reduction Potentials for half-reactions in the *Reference Book of Inorganic Chemistry* by Latimer and Hildebrand. Macmillan, 1929.

the equilibrium would be enormously affected by changing its concentration. In fact the reaction proceeds in the other direction in alkaline solution, the chromium being oxidized and the chlorine reduced. The transition from one to the other may be made by adding  $16\text{OH}^-$  to both sides of the equation. Of these,  $14\text{OH}^-$  will react with the  $14\text{H}^+$ ,  $2\text{OH}^-$  with  $\text{Cr}_2\text{O}_7^{--}$  giving  $2\text{CrO}_4^{--} + \text{H}_2\text{O}$ , and on the right we will have  $2\text{Cr}^{+++} + 8\text{OH}^- = 2\text{CrO}_2^- + 4\text{H}_2\text{O}$ , and  $3\text{Cl}_2 + 6\text{OH}^- = 3\text{ClO}^- + 3\text{Cl}^- + 3\text{H}_2\text{O}$ , with  $2\text{OH}^-$  in excess. Canceling out  $\text{H}_2\text{O}$  and  $\text{Cl}^-$ , and transposing the two sides, we have the equation previously considered in paragraph 13, page 219,

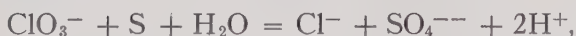


Although this is apparently very different from the equation given above, it involves essentially the same oxidation and reduction steps. On account of the great effect on many of these reactions of varying the concentration of the ions of water, it is well to include in a separate table the reagents which act in alkaline solution. The following brief table may serve for illustration:

Weak	Oxidizing Agents	Strong
$\text{HSnO}_3^-$	$\text{CrO}_4^{--}$	$\text{ClO}^-$
$\text{HSnO}_2^-$	$\text{CrO}_2^-$	$\text{Cl}^-$
Strong	Reducing Agents	Weak

**31. Oxidizing Power and Speed of Oxidation.** There are some substances, like hydrogen peroxide,  $\text{H}_2\text{O}_2$ , which would have great oxidizing power if they could react rapidly enough. It is important to distinguish between an oxidizing agent that is "strong" because it is rapid, and one which is strong but slow. Thus iodine will often react more rapidly than chlorine, and hence produce more oxidation in a given time. Its true oxidizing power, however, is much less, as shown by the fact that it will not oxidize ferrous ion completely, whereas chlorine will. The oxygen acids, like nitric

and sulfuric acids, are not rapid oxidizing agents. This seems to be connected with the fact that they are highly ionized. Nitrous acid, which is not a stronger oxidizing agent in the true sense of the term, is nevertheless a much more rapid oxidizing agent, and is, at the same time, much less dissociated. As we compare the oxygen acids of chlorine, we find that while their reactivity as oxidizing agents decreases in going from  $\text{HClO}$  to  $\text{HClO}_3$ , their strength as acids increases greatly. In a reaction such as the following:

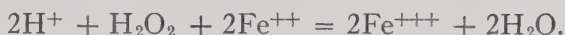


although hydrogen ion appears, whence we might expect it to be favored by decreasing the concentration of hydrogen ion, as a matter of fact it will not take place unless the solution is strongly acid. We may infer from this that  $\text{ClO}_3^-$  is very unreactive, and a large amount of  $\text{H}^+$  must be present in order to give a certain amount of the undissociated strong acid,  $\text{HClO}_3$ , which is reactive. With  $\text{HClO}$ , however, reduction to  $\text{Cl}^-$  will take place rapidly without adding  $\text{H}^+$ , because  $\text{HClO}$  is such a weak acid that most of it is undissociated even in neutral solution. The difference between nitrous and nitric acids may be explained similarly; the latter, being a strong acid, must be rather concentrated in order to give enough undissociated molecules of  $\text{HNO}_3$  to react rapidly. In general, when substances react slowly their true place in the table may not be apparent from their ordinary reactions, and the place assigned may not correspond to a reversible reaction.

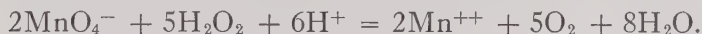
**32. Substances That Can Act Both as Oxidizing and Reducing Agents.** Certain substances appear at two places in the table, corresponding to their power to act either as oxidizing or reducing agents. The way in which they will react depends, of course, upon the nature of the substances with which they are mixed. Thus ferrous ion can be reduced to iron by the action of a very powerful reducing



agent like calcium, or it can be oxidized to ferric ion by the action of a strong oxidizing agent like chlorine. Iodine may be reduced to iodide or oxidized to iodate according, respectively, as it reacts with a reducing agent stronger than iodine or an oxidizing agent stronger than iodate ion. Hydrogen peroxide, not shown in the table because of the irreversibility and slowness of its reactions, may act as an oxidizing agent with some substances themselves capable of oxidation. In these cases the oxygen in the hydrogen peroxide is reduced, as illustrated by the reaction,



On the other hand, in the presence of a sufficiently strong oxidizing agent, the oxygen in the peroxide may be oxidized to free oxygen, as illustrated by the reaction,



**33. The Solution of Insoluble Sulfides.** In Chapter XIII it was shown how certain metallic sulfides could be separated by controlling the hydrogen ion concentration, and it was pointed out that there is a group of sulfides so insoluble in water that even moderately concentrated hydrochloric or sulfuric acids will not sufficiently remove the sulfide ion,  $\text{S}^{--}$ , to make the metallic ion concentration large. To dissolve such sulfides it is necessary to remove the sulfide ion more completely. This is possible by the use of a strong oxidizing agent, usually nitric acid, which changes the  $\text{S}^{--}$  completely into S or even  $\text{SO}_4^{--}$ . Moderately concentrated hot nitric acid, accordingly, will dissolve  $\text{CuS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{PbS}$  and  $\text{Ag}_2\text{S}$ .

The solubility of mercuric sulfide is so extremely low, however, that nitric acid is practically without effect. To dissolve it aqua regia is necessary, the effectiveness of which depends upon the greater speed of reaction of chlorine as compared with nitric acid, and also upon the presence of the chloride ion, which unites with the mercuric ion to form

undissociated mercuric chloride. The aqua regia thus attacks both constituents of the mercuric sulfide instead of only one.

**34. Storage Batteries.** Other reactions besides the simple change between metals and their ions can be utilized in generating an electric current. A very important one is that occurring in the lead storage battery. The reaction utilized is the following:



It is carried out so that the oxidation of the lead to lead sulfate,



takes place at one electrode and the reduction of lead dioxide to lead sulfate,

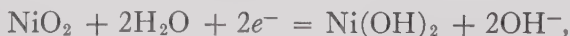


takes place at the other electrode. The electrons travel through the metallic part of the circuit from one electrode to the other. To charge the cell the reaction is reversed by sending a current through the cell in the opposite direction. From the equations it may be seen that the more concentrated is the acid the more is the equilibrium shifted in favor of  $\text{PbSO}_4$ , hence the larger the free energy of the reaction and the electromotive force of the cell. There are other considerations, however, which we have not room to consider here, which argue against too concentrated an acid.

**35.** The nickel-iron storage battery utilizes the following reaction, taking place in alkaline solution:



The electrode reactions are

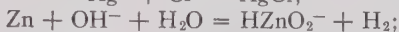
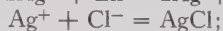
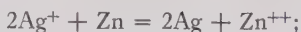


and



## EXERCISES

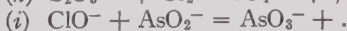
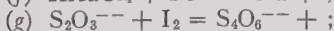
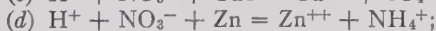
1. In the following reactions state which elements are oxidized and which are reduced:



2. Write equations for the following reactions: zinc plus chlorine to give zinc ion plus chloride ion; stannous ion plus bromine to give stannic ion plus bromide ion; ferric ion plus stannous ion to give ferrous ion plus stannic ion; hydrogen sulfide plus iodine to give sulfur plus hydrogen ion plus iodide ion; cupric ion plus iodide ion to give cuprous iodide (ppt.) plus iodine.

3. Write equations for the reactions between: (a) cupric oxide and hydrogen; (b) cupric oxide and hydrogen ion; (c) cuprous oxide and oxygen; (d) magnesium and hydrogen ion; (e) cupric ion and zinc to give copper; (f) copper and cupric ion; (g) silver ion and zinc. State in each case which elements are oxidized and which are reduced.

4. Complete the following incomplete equations:



5. What is meant by "noble" metals and "base" metals?

6. From the metals given in the table on page 220, construct the battery that would give the greatest electromotive force.

7. Explain how contact with zinc protects iron from corrosion.

8. How can you tell whether a metal will dissolve in any of the following reagents: water, hydrochloric acid, nitric acid, sulfuric acid, sodium hydroxide?

9. How is the oxidizing power of  $\text{H}^+$  affected by its concentration?

10. Explain the cleaning of silver by zinc or by aluminum.

11. How would you prepare each of the following:

(a)  $\text{Br}^-$  from  $\text{Br}_2$ ; (b)  $\text{HCl}$  gas from  $\text{Cl}_2$ ; (c)  $\text{I}_2$  from  $\text{NaI}$ ; (d)  $\text{PbCrO}_4$  from  $\text{Pb}$  and  $\text{CrCl}_3$ ; (e)  $\text{Fe}$  from  $\text{FeCl}_3$ ; (f)  $\text{Fe}(\text{OH})_2$  from  $\text{Fe}$ ; (g)  $\text{Fe}_2\text{O}_3$  from  $\text{FeSO}_4$ ; (h)  $\text{Mn}(\text{OH})_2$  from  $\text{MnO}_4^-$ ; (i)  $\text{HgCl}$  from  $\text{HgCl}_2$ ; (j)  $\text{Hg}$  from  $\text{HgCl}_2$ ?

12. What new substances, if any, would be found and in what amounts upon bringing together the following substances? All ions are in water solution:

- (a)  $\text{Ag}^+$  (1 mole),  $\text{Cu}$  (1 mole) and  $\text{Zn}$  (1 mole);
- (b)  $\text{Ca}$  (1 mole) and  $\text{Cl}^-$  (1 mole);
- (c)  $\text{Cl}_2$  (1 mole),  $\text{Br}^-$  (2 moles) and  $\text{I}^-$  (2 moles);
- (d)  $\text{Fe}$  (3 moles),  $\text{Fe}^{+++}$  (1 mole) and  $\text{Zn}^{++}$  (2 moles);
- (e)  $\text{Zn}$  (1 mole),  $\text{I}_2$  (2 moles) and  $\text{Ag}$  (1 mole).

13. What substance will be present and, if in solution, at what approximate concentrations, in the following cases?

- (a) 1 mole of  $\text{FeCl}_3$ , 4 moles of  $\text{SO}_2$  and 10 moles of  $\text{HCl}$  are mixed in 10 liters of water.
- (b) 1 mole of  $\text{H}_2\text{S}$  is passed into 2 liters of a solution containing 0.5 mole of  $\text{CuCl}_2$  and 1 mole of  $\text{HCl}$ .
- (c) 0.2 mole of  $\text{Cl}_2$  is passed into 1 liter of a solution containing 0.5 mole of  $\text{KI}$  and 0.5 mole of  $\text{KBr}$ .

14. From your knowledge of the oxidation states which the determining elements can assume, state which of the following substances are capable of acting as oxidizing agents, which as reducing agents (or both) and give the substance which each will probably form when so acting:

- (1)  $\text{Cl}^-$ ; (2)  $\text{H}_2\text{S}$ ; (3)  $\text{SO}_2$ ; (4)  $\text{H}_2\text{SO}_4$ ; (5)  $\text{Al}^{+++}$ ; (6)  $\text{H}^+$ ; (7)  $\text{H}_2\text{O}_2$ ; (8)  $\text{F}_2$ ; (9)  $\text{F}^-$ ; (10)  $\text{Ag}^+$ ; (11)  $\text{O}_2$ ; (12)  $\text{Hg}^+$ .

15. Which of the following changes would require (a) an oxidizing agent, (b) a reducing agent, (c) some other type of reagent?—

- (1)  $\text{Sn}(\text{OH})_2$  to  $\text{Sn}^{++++}$ ;
- (2)  $\text{HSnO}_3^-$  to  $\text{Sn}^{++++}$ ;
- (3)  $\text{ClO}^-$  to  $\text{Cl}^-$ ;
- (4)  $\text{I}_2$  to  $\text{IO}_3^-$ ;
- (5)  $\text{H}_2\text{S}$  to  $\text{SO}_4^{--}$ .

16. A certain metal will dissolve in dilute  $\text{H}_2\text{SO}_4$ . Will it dissolve in a solution of  $\text{Cu}^{++}$  or not? Explain.

17. Plan an experiment to determine whether  $\text{Fe}^{++}$  or  $\text{I}^-$  is the stronger reducing agent. ( $\text{Fe}^{++}$  on oxidation becomes  $\text{Fe}^{+++}$  with a change in color.)

18. Plan an experiment to determine whether  $\text{F}^-$  or  $\text{Cl}^-$  gives up its electron more readily.

19. State what electron change takes place (a) when metallic calcium dissolves in water, (b) when magnesium burns in air.

20. The following reactions are known to occur as read from left to right:

- (a)  $2\text{Fe}^{+++} + 2\text{I}^- = 2\text{Fe}^{++} + \text{I}_2$ ;
- (b)  $2\text{Br}^- + \text{Cl}_2 = 2\text{Cl}^- + \text{Br}_2$ ;
- (c)  $2\text{Fe}^{+++} + \text{Sn}^{++} = 2\text{Fe}^{++} + \text{Sn}^{++++}$ ;
- (d)  $\text{Cl}_2 + 2\text{Fe}^{++} = 2\text{Fe}^{+++} + 2\text{Cl}^-$ .

What can you conclude *from these data alone* about the occurrence of the following reactions?—

- (1)  $2\text{I}^- + \text{Br}_2 = \text{I}_2 + 2\text{Br}^-$ ;
- (2)  $2\text{Br}^- + 2\text{Fe}^{+++} = 2\text{Fe}^{++} + \text{Br}_2$ ;
- (3)  $\text{Cl}_2 + \text{Sn}^{++} = \text{Sn}^{++++} + 2\text{Cl}^-$ ;
- (4)  $\text{Sn}^{++} + \text{I}_2 = \text{Sn}^{++++} + 2\text{I}^-$ . Explain your answer.

21. (a) Sketch the arrangement of a battery in which the reaction between Zn and  $\text{Cl}_2$  is used to generate an electric current; (b) from which electrode will the electron stream flow in the wire? (c) How will the e.m.f. of the cell be affected by changing the pressure of  $\text{Cl}_2$ ? (d) How will the e.m.f. be affected by increasing the temperature? Justify your answers.

22. Construct an electric battery to utilize the reaction:



and write the equations for the separate electrode reactions.

23. An electric cell is constructed by placing a zinc electrode in a solution of  $\text{ZnSO}_4$  and an iron electrode in a solution of  $\text{FeSO}_4$ . The solutions are separated by a porous partition. (a) Write the reaction which takes place when the two electrodes are connected by a copper wire. (b) In which direction will the negative electrons flow through the wire? (c) In which direction will the  $\text{SO}_4^{--}$  move through the solution?

24. A battery is composed of an electrode of Zn dipping into a solution of  $\text{ZnSO}_4$  contained in a porous cup. This cup is surrounded by a solution of  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{FeSO}_4$ , and in the latter is a carbon rod to serve as an electrode. (a) Write the equation for the reaction occurring when the cell discharges; (b) how would the electromotive force change with increasing concentration of (1)  $\text{ZnSO}_4$ , (2)  $\text{Fe}_2(\text{SO}_4)_3$ , (3)  $\text{FeSO}_4$ ?

25. In the cell  $\text{Zn}/\text{Zn}^{++}/\text{Ag}^+/\text{Ag}$ , what weight of silver will deposit when 0.654 g. Zn dissolves?

26. Which of the following oxidizing agents are stronger in the presence of 0.1  $N\text{-H}^+$  than in the presence of 0.01  $N\text{-H}^+$ , which are weaker, and which are unaffected by changing concentration of  $\text{H}^+$ ?—

- (a)  $\text{Fe}^{+++}$ , (b)  $\text{I}_2$ , (c)  $\text{IO}_3^-$ , (d)  $\text{MnO}_4^-$ , (e)  $\text{Ag}^+$ . Justify your answers.

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# Chapter XVI

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## *The Constitution of the Atom*

1. The search for the elementary particles constituting matter is as old as science itself. Steadily the size of the supposed ultimate building blocks has decreased until today we speak freely of the structure of the atoms themselves (which were the main elementary units of a generation or two ago). At present only one of the particles in the atom (the nucleus) is supposed to be complex itself and we have reason to believe that we have reliable information even as to its structure. However, it seems certain that the search will continue almost indefinitely even beyond our present advanced stage. It appears probable, though, that as we proceed to more fundamental analyses our present picture of the atoms themselves will be altered little in a practical way, because of our almost complete success in explaining the known chemical properties (*i.e.*, compound formation, etc.). In other words, the one particle in the atom known to be complex, the nucleus, has little effect on the properties of the atom as a whole. This does not detract from the importance of continuing the search, however, for we still have the great cosmological questions to answer: "How was our earth and, in fact, the whole universe made?" "What is the probable future of the universe and in particular the solar system?" "What is the source of the tremendous amount of energy emitted by the sun and other stars?" and numerous other problems. On all of these the properties of the atomic nuclei appear to have



immediate bearing, as we shall see briefly later in this chapter. Also, we should remember the well-known fact that very practical results sometimes are obtained from the most fundamental researches in pure science, for example, the uses of X-rays and radium in medicine.

**2. The Structure of the Atom.** Near the end of the nineteenth century laboratory electrical technique had developed to a point where it was possible to measure electrical forces easily and to produce rather high energy spark discharges conveniently. Immediately several fundamental discoveries were made. Among these were the following. When an electric discharge is sent through a highly evacuated tube provided with sealed-in electrodes, there is given off from the cathode a characteristic discharge called **cathode rays**. Unlike light, these rays are almost entirely stopped by the glass walls of the tube, producing a fluorescence upon the glass where they strike. A screen of fluorescent material like zinc sulfide, if put into the tube in the path of the rays, shows a brilliant fluorescence, very useful in studying these rays. They are deflected from a straight path by either a magnetic or an electric field, in such a way as to indicate that they consist of streams of negatively charged particles, moving with great velocity, which have been called **electrons**.

**3.** By measuring the extent of this deflection by both kinds of field, it has been possible to calculate the ratio of the charge on each electron to its mass, and also the speed of the electrons. It is evident that some such calculation should be possible, because any moving body can be deflected from a straight line by a known force to an extent dependent upon its mass and its speed. It obviously takes more force to deflect a swiftly moving bullet than a slowly moving golf ball, and still more force to deflect the heavy shell of a big gun.

The result of these measurements and calculations, carried out by J. J. Thomson, shows that the speed of the elec-

trons ranges from 10,000 to 100,000 miles per second, a speed approaching that of light, which is 186,000 miles per second. The ratio of the charge to the mass of the electrons is found to be 1850 times the corresponding ratio for a hydrogen ion, which is 96,500 coulombs per gram. Therefore, either the mass of the electrons is less, or the charge is greater than that of a hydrogen ion. Now it has been found that the charge is the same (though opposite in sign), hence we are led to the conclusion that the mass of the electron is  $\frac{1}{1850}$  of that of the hydrogen ion, the smallest particle of matter previously known.

The discovery of the electron provided a unit with which atoms may be constructed, and the fact that the nature of the electrons composing the cathode stream is entirely independent of the nature of the cathode used, as well as of the residual gas in the tube, indicates that atoms of all substances contain the same kind of electrons.

4. In addition to the electrons liberated by all substances in a spark discharge, there are produced **positively charged heavy particles** of different masses for each element or compound. For example, if the noble gas, krypton, is placed in the discharge tube, six heavy, singly positively charged particles, six doubly charged, and perhaps even six triply charged will be produced (the relative intensities of the groups with different charges depending on the violence of the discharge and the pressure of the gas). When the masses of the particles are measured in the way described above for the electron they are found to be 78, 80, 82, 83, 84 and 86, the same six appearing in each group and the relative numbers in each of the three groups being exactly the same. The interpretation is that the element, krypton, is a mixture of six different atoms having the different weights given but the same tendency to become positively charged in the discharge (*i.e.*, the same tendency to lose electrons). The relative abundances of the different atoms, called **isotopes**, are determined by direct measurement of

TABLE 1  
STABLE ISOTOPES OF THE ELEMENTS

ELE- MENT	MASS NO.	ELE- MENT	MASS NO.	ELE- MENT	MASS NO.	ELE- MENT	MASS NO.	ELE- MENT	MASS NO.	ELE- MENT	MASS NO.
H	1	Sc	45	Br	79	Cd	106	La	139	Hf	176
	2		46		81		108		136		177
			47		78		110		138		178
			48		80		111		140		179
He	4	V	49	Rb	82	In	112	Pr	142	Ta	180
Li	6		50		83		113		141		181
	7		51		84		114		142		182
Be	9		50		86		116		143		183
B	10	Cr	52	Sr	85	Sn	113	Nd	144	Re	184
	11		53		87		115		145		186
C	12		54		84		112		146		185
	13		55		86		114		148		187
N	14	Mn	54	Y	87	Zr	115	Sm	150	Os	186
	15		56		88		116		144		187
O	16		57		89		117		147		188
	17		58		90		118		148		189
F	18	Co	57	Mo	91	Sb	119	Eu	149	Ir	190
	19		59		92		120		150		192
Ne	20		58		94		122		152		191
	21		60		96		124		154		193
Na	22	Ni	61	Cb	93	Te	121	Gd	151	Pt	192
	23		62		92		123		153		194
Mg	24		64		94		120		155		195
	25		63		95		122		156		196
Al	26	Zn	65	Ru	96	I	123	Tb	157	Au	198
	27		64		97		124		158		197
Si	28		66		98		125	Dy	160		196
	29		67		100		126		159		198
P	30	Ga	68	Ma	—	Xe	128		161	Hg	199
	31		70		96		130		162		200
S	32		69		98		127		163		201
	33		71		99		124		164		202
Cl	34	Ge	70	Rh	100	Cs	126	Ho	165	Tl	204
	35		72		101		128		166		203
A	37		73		102		129		167		205
	36		74		104		130	Er	168	Pb	204
K	38	As	76	Pd	101	Ba	131		170		206
	40		75		103		132		169		207
Ca	39		74		102		134	Tm	171	Bi	208
	40		76		104		136		172		209
	41	Se	77	Ag	105	Lu	133		173	Th	232
	42		78		106		130		174		235
	43		80		108		132		176		238
	44		82		110		134		175		
					107		135		176		
					109		136				
							137				
							138				

the relative numbers in the different charge groups and are found to be

$\text{Kr}^{78}$ , 0.42%;  $\text{Kr}^{80}$ , 2.45%;  $\text{Kr}^{82}$ , 11.79%;  $\text{Kr}^{83}$ , 11.79%;  
 $\text{Kr}^{84}$ , 56.85%;  $\text{Kr}^{86}$ , 16.70%;

TABLE 2  
 RELATIVE ABUNDANCE OF CERTAIN ISOTOPES

ELEMENT	MASS NO.	RELATIVE ABUNDANCE
H	1	99.98
	2	0.02
Li	6	7.9
	7	92.1
B	10	20.6
	11	79.4
O	16	99.76
	17	0.04
	18	0.20
Ne	20	90.00
	21	0.27
	22	9.73
Cl	35	76
	37	24
K	39	93.2
	40	0.012
	41	6.8
Cu	63	68
	65	32
Zn	64	50.9
	66	27.3
	67	3.9
	68	17.4
	70	0.5
Br	79	50.7
	81	49.3

giving an average of 83.7 for the weight of the average Kr atom. (This method of determining atomic weights has come to be as accurate as the older method of measuring out a gram-atom of element and weighing it.) Similar experiments on the other elements have shown most of them to be mixtures of two or more isotopes, as shown in Table 1.

We notice that even hydrogen has two isotopes, the ordinary isotope of mass one and a rare one of mass two, called **deuterium**. In this case the masses differ by two-fold, a larger factor than in any other case, and we are in an excellent position to decide whether the mass of the atom plays a fundamental rôle in the chemical properties of the atom. Table 3 shows the properties of a series of compounds of the two isotopes. D is the symbol used for the heavier isotope. Evidently the mass effect is small even in this case so we conclude that somehow the mass of an atom is not fundamental to its chemical properties.

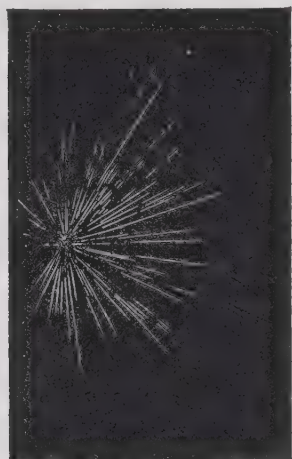
TABLE 3

COMPARISON OF CHEMICAL PROPERTIES OF THE HYDROGEN ISOTOPES

	MASS ONE ISOTOPE HYDROGEN	MASS TWO ISOTOPE DEUTERIUM
Relative ionization potentials of atom (arbitrary unit) . .	1.000000	1.000270
Heat of dissociation of mole- cules, H <sub>2</sub> , D <sub>2</sub> . . . . .	101,900 calories	103,700 calories

5. In order to understand this fact we must consider certain experiments on the collisions between ordinary slowly moving atoms and high velocity, doubly positively charged helium atoms, called **alpha particles**. At about the same time that the experiments described above on spark discharges through gases were begun, it was discovered that certain of the elements spontaneously emit radiations, among which are heavy high velocity particles of double positive charge and mass 4, which we now know to be helium atoms which are lacking two electrons.

By virtue of their high energy, it was possible to detect these bodies one at a time and to record their progress through matter until they had lost most of their energy through collision with ordinary atoms. (This occurs after they have traversed between 2 and 5 cm. of ordinary air, the distance varying, of course, with the energy of the particular alpha particle.) If one fills a glass cylinder



Track of  $\alpha$ -rays.



Track of two  $\alpha$ -rays (enlarged).

FIG. 1.

which has a movable bottom with moist air and alternately moves the bottom of the cylinder up and down, one sees lines of water droplets form on the down stroke if there is a small amount of some alpha emitting substance such as the element polonium on the wall of the vessel. This beautiful apparatus, called a "cloud chamber," invented by C. T. R. Wilson, enables one to study the phenomena visually, in an intimate way.

Figure 1 shows two photographs of such tracks, the one on the right containing a track having sharp changes of direction such as collisions with heavy bodies in the air would



cause. The gas laws have taught us how to calculate the approximate size of the molecules as well as the number in a given volume under any conditions. Consequently, as soon as tracks like the one in Fig. 1 were observed, calculations were made showing that the alpha particles must have hit a heavy body in the air only once in passing through several thousand atoms. This showed immediately that the mass of the air molecules must be concentrated in small regions having only about  $\frac{1}{10,000}$  the diameter of the atoms themselves. Also, calculations on the angles through which the alpha particle was deflected showed the mass of the body struck to be the known atomic weight of either oxygen or nitrogen, according to which was involved in the particular collision considered. The startling fact therefore was established that somehow the **mass of the atom was concentrated in a very small part of the total atomic volume.** This suggested that the light electrons might be revolving about the heavy, positively charged nucleus in a way similar to that in which the planets revolve around the sun, which we know now to be the case.

6. If a beam of high energy electrons is passed through helium gas, the electrons are found to emerge with their energy practically unchanged unless the energy of the electron exceeds a certain minimum value. As the energy of the beam is increased from a value near zero, one finds no slowing of the electrons until a certain value is reached, when many of the electrons lose nearly all of their energy. This experiment shows that the helium atom is incapable of taking energy in amounts smaller than a certain minimum. It is necessary to hit the atom with at least a certain amount of energy before anything happens. Similar experiments with the other atoms have given similar results, the particular minimum energies being different for each element. This concept that atoms can take energy in certain definite amounts only, together with its numerous consequences, is known as the **quantum theory.**

7. After the atoms in the above experiment have been struck with high energy electrons, they emit light. (This is the mechanism of the familiar neon sign.) The color of this light is found to be definitely related to the minimum

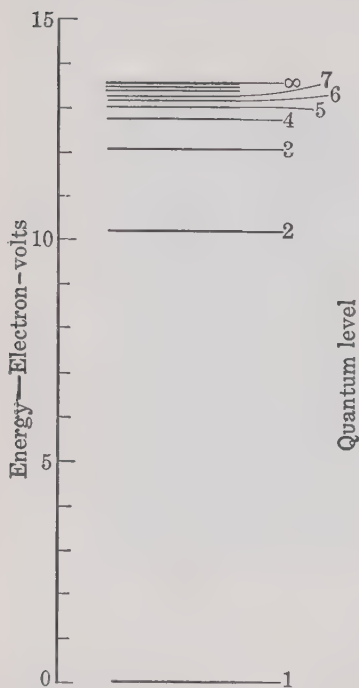


FIG. 2. Energy levels for hydrogen.

energy required to excite the atom, so we conclude that the atom has emitted this "chunk" of energy as light after having taken it from the electron. By using a gas being bombarded with electrons of a wide range of energies and carefully determining the various wave lengths (roughly related to color) of the light emitted, it is possible to decide not only what is the smallest amount of energy a given atom will absorb, but what the successively larger amounts are. In this way one is able to say what values the energy of any given atom can have. This set of values, when written in increasing order, is called the **energy level**

**scheme**. Figure 2 represents the scheme for hydrogen, the distance above the bottom line being proportional to the energy values.

8. The problem of correlating the significant facts we have considered above was solved in its first form in 1913, soon after the experiments on alpha particle collisions had shown the mass of the atom to be concentrated in one position. It was postulated that the electrons in the atom move in orbits around the nucleus, held by the positive charge of the nucleus, and that the different energy states

correspond to the electrons being moved into orbits farther from the nucleus. The values of the energy states of hydrogen were calculated accurately on this model when the orbits were selected by the rule that only those in which the angular momentum (for circular orbits, the product of the mass of the electron and its velocity and the radius of the orbit) of the system would be an integral multiple of a certain fundamental constant. It was this rule for selecting the orbits which actually occur that was so new and illuminating.

The calculation of the energy of an electron rotating in a certain orbit around a nucleus with a given positive charge is quite simple. It is analogous to the calculation of the energy of motion of the earth in its orbit around the sun. Today we have a better idea of the origin of the strange rule which leads to the selection of the particular orbits which occur in atoms but we still find it mysterious and wonderful. The principle involved mainly is that electrons, and in fact all particles, act to varying degrees like light in the way their movements are affected by obstacles in their paths. This point is expressed quantitatively and accurately in a mathematical form which has enabled us to calculate exactly all of the known chemical properties of the hydrogen atom. (The solution of the equations involved is difficult and has been carried through completely only for the simpler atoms, though we are certain the results will be obtained for the others when enough work has been done.)

9. Though we are not in a position here to consider in detail the solution of the problem of atomic structure, certain of its fundamental features will be pointed out. First, the selection of the possible orbits the electrons may fill is such as to give them radii which are approximately some integral multiple of the radius of the innermost orbit ( $0.506 \times 10^{-8}$  cm. for hydrogen). We therefore group the electrons filling orbits of approximately the same radius into "**electron shells**," because, even though plane themselves, the orbits of several electrons oriented in various ways will more or less fill a volume of space of the shape of a spherical shell (the space between two concentric spheres). The number of electrons fitting into each shell is propor-

tional, as we might expect, to the volume of the shell, *i.e.*, it varies as the square of the radius of the shell. Of course the actual size of the shells decreases as the nuclear charge increases and pulls the electrons closer. The number of electrons filling the shell is not decreased, however, because the stronger nuclear attraction enables them to fit more closely, apparently, in just the right way. Since the first shell has two, the next will have  $2 \times 2^2$  or 8 since its radius is twice that of the first shell, the third has  $2 \times 3^2$  or 18, the fourth 32, and the fifth 50. These are the only shells involved in the atoms in their ordinary states, though any atom can have one or more of its electrons knocked into higher shells by collision, after which the electrons will fall back into their old position and the energy will be emitted as light. Table 4 gives the electronic structure of the lighter atoms.

10. The orbits of the individual electrons in atoms are described by three numbers, called **quantum numbers**. The **principal quantum number**,  $n$ , is the number characteristic of the shell being considered, *i.e.*,  $n = 1$  for the first shell,  $n = 2$  for the second, etc. The different electron orbits grouped into a single shell are specified in the mathematical treatment by two additional quantum numbers. One of these, designated by  $l$ , is concerned with the **shape** of the orbit. The orbits are circles when  $l = n - 1$ , and have elliptical shapes when  $l$  is different from  $n - 1$ . The other number, designated by  $m$ , is associated with the position in space of the plane of the orbit. The mathematical treatment shows that  $l$  can have all integral values from 0 to  $n - 1$  and  $m$  can have all integral values from  $-l$  to  $+l$ , including zero. These rules, with the additional rule that in a given atom only two electrons can have any one set of values for  $n$ ,  $l$  and  $m$ , allow us to build up the electronic structure of the atoms and account for the maximum number of electrons 2, 8, 18, etc., that can exist in any one principal shell. We can think of the two electrons which are allowed to have the same values for  $n$ ,  $l$  and  $m$  as not being strictly identical but as spinning in opposite directions. Experimentally, we know that all electrons behave as though they were spinning rapidly, the momentum involved being just one half of the fundamental unit mentioned previously in connection with the selection of the allowed orbits in the hydrogen atom. Other particles behaving in a similar way are the proton, neutron and positive electron.

In the case of  $n = 1$ , the only value  $l$  or  $m$  can have is zero, so we are allowed only 2 electrons in the first shell. For  $n = 2$ , the possible values

TABLE 4  
ELECTRON STRUCTURE OF ATOMS

Element	H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	A
Atomic number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Electrons in 1st level	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Electrons in 2d level	1	2	2	2	2	2	2	2	2	2	8	8	8	8	8	8	8	8
Electrons in 3d level			1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8
Element	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Atomic number	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Electrons in 1st level	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Electrons in 2d level	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
Electrons in 3d level	8	8	8	9,8	10,8	11,8	13,8	14,13	15,14	16,15	18,17	18	18	18	18	18	18	18
Electrons in 4th level	1	2	3	3,4	3,5	3,6	2,7	2,3	2,3	2,3	1,2	2	3	4	5	6	7	8

of  $l$  are 0 and 1. With  $l = 0$ , the only possible value for  $m$  is 0 so 2 electrons can have  $l = 0$ , while  $l = 1$  allows three values of  $m$ , for each of which 2 electrons are permitted, giving a total of 6 electrons. Adding, we get 8 electrons permitted for the second shell. Similar treatment of the other shells gives 18 for the third, 32 for the fourth and 50 for the fifth.

The different electrons have been assigned names according to their shell and  $l$  quantum number. Electrons with  $l = 0$  are called *s*-electrons; with  $l = 1$ , *p*-electrons, and so on, the order being *s*, *p*, *d*, *f* and *g*. The shell is designated by a number in front of the letter name. For instance, 3*s* means one of the two electrons having  $l = 0$  in the third shell. Table 5 gives the complete electronic structures of a few of the atoms.

**11.** The tendency for an atom with several electrons to have them grouped together into shells, each having a definite number of electrons, is fundamental to the study of chemical reactions. **The essential cause of chemical bond formation is the tendency of two or more atoms, each of which has a few electrons not in filled shells, called valence electrons, to redistribute their electrons among themselves in a way that as nearly as possible places all electrons in filled shells.** For example, two hydrogen atoms combine by **sharing their two valence electrons** so both electrons can belong to a closed shell of two, at least part of the time. (We may think of the electrons moving around first one proton and then the other, this interchange occurring so rapidly that neither proton has time to get away before the electrons move over to it.) This is one of the two basic kinds of chemical bond and is known as the **electron-share**, or **electron-pair bond**, for obvious reasons. It is represented by placing two dots representing the shared valence electrons between the bound atoms, *e.g.*, **H:H** for H<sub>2</sub> molecule. The other bond results when an atom (non-metal) whose valence shell lacks just one or two electrons takes the valence electrons from an atom having only one or two (metal). The result of this transfer is a negative charge on the atom gaining electrons and a positive charge on that losing its valence electrons and the bond consists of the





standard electrical attraction between these charges so produced. For example, a sodium atom having one valence electron gives it to a fluorine atom having seven valence electrons to fill up the second shell on the fluorine atom to its proper value of eight forming the NaF molecule represented by  $\text{Na}:\ddot{\text{F}}:$  or  $\text{Na}^+\text{F}^-$ . This is known as the **electrostatic** or **ionic bond** because of its electrical character.

12. These two bonds differ greatly, in fundamental ways. The electron-pair bond, consisting as it does of a sharing of electrons to close two electron shells, one on each atom, should be broken if the distance between the bound atoms were increased by more than about the thickness of the average electron shell, a few tenths of an Ångstrom, which is  $10^{-8}$  cm. Furthermore, one would expect the rupture to occur rather suddenly as the distance is increased, much as a cast iron rod breaks if sufficient tension is applied to its ends. On the other hand, since the electrostatic bond is of the nature of an attraction between two charged bodies, increasing the distance of separation by a factor of two (about two Ångstroms) should decrease the bond strength by only a factor of  $2^2$ , or 4, due to the inverse square law of force applying in this case. This makes the electrostatic bond much more elastic in character, and allows molecules with such bonds to be formed and broken more rapidly because the collisions which can lead to formation and destruction do not have to be so exactly right as in the case of the molecules with electron-pair bonds. In other words, we expect from these considerations to find that molecules with electron-pair bonds can have more definite structures and that, though their formation and destruction may involve no more energy (in fact, generally less) than for those with electrostatic bonds, they will be formed and destroyed less readily due to the exactness with which the atoms have to be placed. All of these are well-known facts and verify our whole picture. It is interesting

that the most essential molecules in living organisms are of the electron-pair type.

13. Certain media, such as water, are able to reduce the force acting between charged bodies by a certain factor called the dielectric constant (cf. Chapter VIII, paragraph 2). The dielectric constant of water is 80, so we expect that molecules held together by electrical bonds will be broken into their charged fragments when they are dissolved in water or any other liquid of high dielectric constant, the mild collisions occurring due to thermal motions of the molecules in the liquid being sufficient to break the weakened bonds. This is the explanation of the phenomena of ionization we have studied in preceding chapters and gives us an immediate and practical test for bond type.

14. Intermediate between the two types of bond just considered, there is a large and important class of molecules (cf. Chapter V, paragraph 12) in which the electrons are incompletely transferred. For instance, they may spend three fourths of their time on one atom and one fourth on the other, giving us a bond half of the share type and half of the electrostatic type. These bonds of intermediate type, called **polar bonds**, have characteristics intermediate between those discussed above for the pure types. For example, compounds with bonds of this kind may ionize only partially when dissolved in water, constituting the general class of weak electrolytes. Finally, it must be noted that a single molecule may have different types of bonds in its different parts, for instance, in  $\text{Na}_2\text{SO}_4$  the bonds between the Na and O atoms certainly are electrostatic while those between the S and O atoms are electron-share bonds.

15. Examination of Table 6 reveals that A has only 8 electrons in its third shell, which should have 18 when filled. Argon certainly is an extremely inert element, so we are forced to consider why atoms with three shells of electrons are relatively satisfied when their third shell has 8 instead of 18 electrons. When we consider the courses

TABLE 6  
 ELECTRON STRUCTURES OF NOBLE GAS ATOMS

	He	Ne	A	Kr	Xe	Rn
At. No. . . .	2	10	18	36	54	86
Difference . .	8	8	18	18	32	
1st level . . .	2	2	2	2	2	2
2d " . . .		8	8	8	8	8
3d " . . .			8	18	18	18
4th " . . .				8	18	32
5th " . . .					8	18
6th " . . .						8

of action open to the A atom, the impossibility of filling the shell by either kind of chemical bonding becomes clear. By complete transfer of electrons, the A atom has the choice of losing 8 or gaining 10, in either case the charges induced after the removal, or gain, of say 5 electrons, would be so large as to prevent any further transfer. The possibilities through sharing of valence electrons with other atoms appear to be better, but when we realize that about ten other atoms must be grouped around the A atom to fill the 18 shell, we see that this possibility is ruled out because no known ten atoms can be fitted around A closely enough to form electron-share bonds, which are particularly sensitive to structural inconveniences anyway. So it becomes apparent that for the larger shells it is not the shell itself which will be filled by chemical bonding, but rather some smaller group within these larger shells. This group is that of **eight**. It is more stable than any other grouping of electrons within the shell, and, for the reasons presented above, assumes the rôle for bond formation played by the shell as a whole in the lighter atoms. In fact the whole principle of bond formation can be restated in the form that **bonds are formed to complete outer shells or octets**.

16. The Periodic System itself affords abundant justification for this treatment of the octet as a particularly stable sub-group in the larger shells. For example, when one more electron is added to the argon structure to form potassium,

instead of going into the third shell, which needs 10 more, it prefers to go into the empty fourth shell. This continues till the fourth shell has three, when the next electron put in (to form Ti) sometimes goes into the third shell. This happens repeatedly until the third shell is finally filled in Cu, which has one electron in the fourth shell. The possibility of having the electrons in either of two shells leads to an atom's having more than one possible set of valence electrons and therefore two or more sets of chemical properties. This, of course, is known to be true of just these elements we have discussed and also of those involved in the same way in the filling of the fourth shell while the fifth has only a few electrons in it.

## ATOMIC NUCLEI

**17. Introduction.** In the preceding paragraphs it has been shown that the only property of the nucleus which is of practical importance to the ordinary chemical characteristics of the atom is the positive charge. However, we know much more about the nuclei than the values of their charges and we shall consider their general properties briefly in this section.

At present, approximately 480 nuclei are known. Of these, 261 are stable, or last at least as long as  $10^{12}$  years, and the remainder decompose at various rates to form the stable nuclei. It seems probable that a few more stable nuclei will be found and almost certain that additional unstable ones will appear, so we may expect the total somewhat to exceed 500 in the rather near future.

**18.** The principal constituents of the nuclei now appear to be the proton and the **neutron**. The proton is the nucleus of the ordinary hydrogen atom, has a mass of 1.0076 and a single positive charge. **The neutron has no charge and weighs 1.0090.** These particles apparently exist together in the nuclei in a way quite analogous to the way the molecules exist in a small drop of liquid, or perhaps a very

small crystal. The densities of the nuclei correspond to what would be expected from the masses and sizes of the neutron and proton if they were packed closely together. Also, the observation from collision experiments that only at relatively short distances (of the order of the diameter of the average nucleus,  $10^{-12}$  cm.) do the constituents strongly attract each other leads us to expect that they must be extremely close together in order to account for the

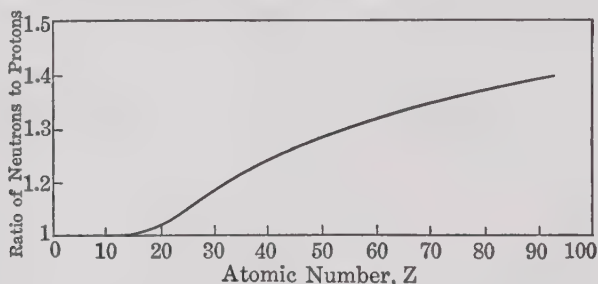


FIG. 3.

great stability of the ordinary nuclei. The nature of the attraction appears to be such that the **most stable structures tend to have about equal numbers of neutrons and protons**. This gives the well-known rule that the atomic weights of the elements are nearly twice the atomic numbers. However, as the nucleus increases in size the strong repulsive forces acting between the protons at these short distances (such electrical forces vary as the square of the reciprocal of the distance of separation) seems to drive off some of the protons, so that the stabler heavy nuclei have somewhat fewer protons than neutrons. Figure 3 shows this.

19. When the nuclei are heated by bombardment with high energy particles, such as protons, neutrons, alpha particles, the nucleus of the heavy hydrogen isotope (called the **deuteron**), or high energy light (called **gamma rays** or **hard X-rays**) the energy apparently is distributed rather rapidly over the system as a whole and results in an evaporation process causing certain simple particles, such



as neutrons, protons, deuterons or alpha particles, to boil off until the system has cooled. These energies correspond to nuclear temperatures of several hundred million degrees. Loss of the energy by the emission of gamma radiation also occurs. There are differences in mechanism among the various processes which lead to systematic differences in the rates at which these emissions occur.

**20.** The rate of the evaporation process decreases very sharply with the temperature of the nucleus, so that if the cooling process following bombardment with high energy particles happens to leave the nucleus in a slightly warm condition (as it may if there is only enough energy to evaporate, say, one particle but not two, or two particles but not three, etc.) the rate at which it cools may become very small and may increase the time of cooling from about  $10^{-13}$  seconds (for the rapid evaporation processes following bombardment) to  $10^{12}$  years. These slower processes of course are almost in a different class, experimentally, because they may be detected at convenient times after bombardment rather than requiring investigation during bombardment. The whole set of phenomena associated with these slower transformations is known as **radioactivity**.

**21. Types of Radioactivity.** When nuclei with the ratio of protons to neutrons somewhat lower than the stable value are formed in a state not too highly excited, the return to the stable state does not occur through the evaporation of a neutron, but through the conversion of a neutron into a proton in the nucleus with the **emission of a negative electron**, and possibly other radiation whose existence we suspect but have not confirmed. This process is known as **beta radioactivity**. For example, the unstable  $\text{Na}^{24}$  nucleus has 13 neutrons and only 11 protons, while the stable  $\text{Mg}^{24}$  has 12 neutrons and 12 protons. As a consequence,  $\text{Na}^{24}$  emits electrons, increasing the nuclear charge from +11 to +12, changing the chemistry from that of Na to Mg and forming the stable  $\text{Mg}^{24}$  isotope. Half of any given

amount of this  $\text{Na}^{24}$  changes in this way in 14.8 hours the **half-life of the radioactivity**.

22. In the other case, for which the proton to neutron ratio is too high, there are three processes which can lead to stability from low states of excitation. One is **alpha particle emission**, which is most effective in readjusting the ratio when the stable ratio is considerably less than unity, *i.e.*, for heavy elements. This is what one expects, because subtracting 2 neutrons and 2 protons helps the ratio most under these conditions. It is a fact that nearly all alpha radioactivities occur in nuclei with masses of 200 or more. The alpha particle is not quite as hard to tear away as the proton because it is itself a very stable nucleus. However, alpha radioactivity in general requires somewhat warmer nuclei than do the other kinds of radioactivity. Another and more common course taken by these excited nuclei is the emission of a positive electron, called **positron**.

23. The positron has the same characteristics as the electron except that its charge is positive. It does not exist at any appreciable concentration because it reacts immediately (life of about  $10^{-4}$  seconds in ordinary matter) with a negative electron to turn both itself and the ordinary electron into gamma radiation. It is possible to reverse this **annihilation process** by sending gamma radiation through some heavy element like Pb. Sometimes, when the conditions are just right, the high electrical forces near the Pb nuclei help tear the gamma rays apart, the negative electron being attracted to the nucleus and the positron being repelled. Figure 4 is a picture of such an event taken in a Wilson cloud chamber. The whole apparatus was placed in a magnetic field which makes electrons move in circles, the direction depending on the sign of the charge on the electron. Here we see one moving in one direction and the other in the opposite. They originate from the same point and obviously have practically the same energy since the size of the circle measures the energy.

The **positron radioactivity** is in every way analogous to the ordinary negative electron activity except that the positrons are annihilated by surrounding matter to form gamma radiation, so we always have this gamma radiation associated with positron beta activity.



FIG. 4. Stereoscopic cloud chamber photographs of an electron-positron pair ejected from a 1 mm. lead foil by the gamma radiation from boron bombarded by protons. (This photograph was furnished through the courtesy of Dr. Charles C. Lauritzen.)

24. The third way in which a high proton to neutron ratio can be cured is by the nucleus apparently swallowing one of the nearest electrons, from the first shell of two, to convert a proton into a neutron. We do not believe ordinary electrons can exist as such in nuclei, since they are larger than nuclei, hence we think of this as a transformation not only of the proton but of the electron at the same time. This process is known as **K-electron capture** because the first shell of electrons is known as the K shell. The probability of this happening increases as the nuclear charge increases because the electrons are closer. It is difficult to detect, because all we are able to observe is the emission of X-rays, which constitute the high energy light evolved when

one of the electrons from the lower shells is removed and an electron from a higher shell falls into the hole left. However, we have reason to believe the process to be quite important.

**25.** Finally, we must say that the proton to neutron ratio apparently does not completely fix the properties of a nucleus of given mass. In other words, there seem to be several ways of putting a given number of protons and neutrons together to give nuclei of different properties. Such nuclei are called **isomers** and afford us definite evidence of what we may call structural effects in nuclei. The more excited isomer of a pair may change to the other isomer by emission of a gamma ray or both isomers may be beta active, with different half-lives, of course, forming the same final nucleus.

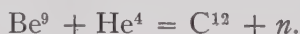
**26.** Table 7 contains facts about some of the more important radioactive nuclei, those with asterisks being found

TABLE 7  
SAMPLE RADIOACTIVITIES

ISOTOPE	HALF-LIFE	TYPE OF RADIATION	PRODUCT
He <sup>6</sup>	0.7 sec.	$e^-$	Li <sup>6</sup>
N <sup>13</sup>	10.3 mins.	$e^+$	C <sup>13</sup>
Na <sup>22</sup>	3 yrs.	$e^+$	Ne <sup>22</sup>
Na <sup>24</sup>	14.8 hrs.	$e^-$	Mg <sup>24</sup>
P <sup>32</sup>	14.5 days	$e^-$	S <sup>32</sup>
S <sup>35</sup>	80 days	$e^-$	Cl <sup>35</sup>
*K <sup>40</sup>	$1.4 \times 10^9$ yrs.	$e^-$	Ca <sup>40</sup>
Mn <sup>56</sup>	2.5 hrs.	$e^-$	Fe <sup>56</sup>
*Rb <sup>87</sup>	$1 \times 10^{11}$ yrs.	$e^-$	Sr <sup>87</sup>
Br <sup>80</sup> (1st isomer)	4.5 hrs.	$\gamma$	Br <sup>80</sup> (2d isomer)
Br <sup>80</sup> (2d isomer)	18 min.	$e^-$	Kr <sup>80</sup>
Ag <sup>106</sup> (isomer)	7.5 days	$e^-$	Cd <sup>106</sup>
Ag <sup>106</sup> (isomer)	25.5 mins.	$e^+$	Pd <sup>106</sup>
I <sup>128</sup>	25 mins.	$e^-$	Xe <sup>128</sup>
*Sm <sup>148</sup> (?)	$9 \times 10^{10}$ yrs.	$\alpha$	Nd <sup>144</sup> (?)
Au <sup>198</sup>	2.7 days	$e^-$	Hg <sup>198</sup>
*Ra <sup>226</sup>	1600 yrs.	$\alpha$	*RaA
*Th <sup>233</sup>	$1.39 \times 10^{10}$ yrs.	$\alpha$	*MsThI
*U <sup>238</sup>	$4.56 \times 10^9$ yrs.	$\alpha$	*UII

in nature and the rest having been made since the discovery of artificial radioactivity in 1934.

**27. Experimental Technique.** The natural radioactive elements, *e.g.*, radium, supply us with a source of high energy alpha particles quite useful in exciting nuclei for certain purposes. For example, neutrons are conveniently produced from beryllium metal by mixing it with radium, according to the reaction,



However, in general both the energies and intensities of these sources of high energy particles are too low to allow us to study the large number of radioactive nuclei successfully, although artificial radioactivity was first produced this way. The great advances made in this field in the last few years have been largely associated with the development of various devices for accelerating the simpler charged particles to high energies. Perhaps the best known of these is the **cyclotron**, which acts by bending the beam into almost a circle in a strong magnetic field and giving the particles a little electrical push every time they pass a certain region in the circular path. They finally become so energetic that they fly out of the circular path. Actually this occurs gradually so their path is like a spiral. They then hit the target being studied. The other devices mainly depend on the development of very high voltages which will accelerate the particles in one push. These methods have not given energies or intensities as high as the cyclotron but they do give beams of somewhat more definite energy, which are useful for certain experiments. The neutron cannot be accelerated electrically, of course, but it is a very useful disintegration tool because it has no charge and is not repelled by the nuclear charges. Most nuclei readily absorb neutrons and after having taken one are left in an excited state because part of the neutron's mass is converted into energy in the absorption process. The



equivalence of mass and energy is a well-known law which the work in this field has verified completely (cf. Chapter II, paragraph 3). The absorption of a neutron usually leads to negative electron radioactivity for the reasons given in the preceding section.

**28. Applications.** Radioactive nuclei are valuable as tracers in the study of chemical reactions. For example, it has been shown by feeding foods containing radiophosphorus that even the bones in the animals become radioactive in a few days, proving that there are constant sloughing away and building up processes occurring in the live animal. There are other important applications in the use of the radiations to destroy unwanted tissue such as cancer.

**29.** The facts discovered about the nuclei, in particular the tremendous energies involved in their reactions, seem to supply us with a plausible explanation of the source of **stellar energy**. We can see that the sun, for instance, could shine for a period millions of times longer than the age of the earth, which is approximately  $3 \times 10^9$  years, if certain simple nuclear reactions were occurring. In fact, physical measurements on the sun almost require us to believe the temperature at the center to be about  $10^7$  degrees, at which temperatures certain nuclear reactions would undoubtedly occur. The details of stellar constitution and change certainly are not all clear but we feel that we have a good lead.

**30.** Finally, we must mention the determination of the age of the earth by radioactivity. The elements uranium and thorium both are composed entirely of radioactive nuclei, whose rates of decay are known accurately. The products in both cases are lead isotopes, so the amount of lead found in a rock containing a certain amount of uranium or thorium tells us how long it has been since the rock was solidified. This assumes, of course, that no lead was present when the rock formed. Examination of the isotopic constitution of the lead shows whether this is true. The results for the oldest rocks are nearly two billion years.



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# Chapter XVII

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## *The Periodic System of Elements*

1. It became evident to chemists a long time ago that there are certain elements which may be grouped together by reason of their similarity. Among such groups may be mentioned lithium, sodium and potassium, commonly called the alkali metals; calcium, strontium and barium, the alkaline earth metals; fluorine, chlorine, bromine and iodine, called the halogens. In 1866 Newlands read a paper before the London Chemical Society in which he showed that if the then known elements were arranged in the order of increasing atomic weight, as follows:

H	Li	Be	B	C	N	O	F	Na	Mg	Al	Si	P	S	Cl	K	Ca
1	7	9	11	12	14	16	19	23	24	27	28	31	32	35.5	39	40

there is a similarity between every eighth element in the series, so that if it is divided into groups of eight and these placed under each other in successive rows, as follows,

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	etc.			

then the elements standing in the same vertical column are those which correspond to each other in chemical nature. It is evident from the table that this is the case. Strange as it may seem, this discovery was received with some ridicule, and its value not appreciated till later. In 1869 this same idea was more fully elaborated independently by Men-

TABLE 1

# PERIODIC SYSTEM.—MENDELÉEFF (MODIFIED)

[illegible]

TABLE 2

The periodic table is organized into groups and periods. The elements are labeled with their chemical symbols. The table includes the following elements:

- Period 1:** H, He
- Period 2:** Li, Be, B, C, N, O, F, Ne
- Period 3:** Na, Mg, Al, Si, P, S, Cl, Ar
- Period 4:** K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr
- Period 5:** Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe
- Period 6:** Cs, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn
- Period 7:** Fr, Ra, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr

The table is color-coded with various shades of blue, green, and yellow to distinguish between different groups of elements.

deléeff and Lothar Meyer. Each of these chemists tabulated the elements substantially by the method shown in Table 1. The fundamental idea expressed by such an arrangement is that of the periodic recurrence of properties as the atomic weights increase.

2. Various other representations of the Periodic System of elements have been proposed, the most useful of which, given in Table 2, is based upon the facts of atomic structure that have been set forth in the previous chapter, summarized particularly in Tables 4 and 5. This arrangement has been made by listing the elements in order of increasing atomic number, separating them into rows, or periods, each beginning at an alkali metal with a new energy level and ending at a noble gas with a completed energy level. The elements in the several rows which are closely related by reason of their equal numbers of valence electrons are connected by lines and constitute a **group** which is designated by the common number of valence electrons. The periods beginning with K, Rb and Cs, are longer than the preceding two periods because of the building up of the underlying levels, and there appear two elements in each with the same number of valence electrons. The one which more closely resembles the corresponding elements in the first two periods is connected with these by a full line and is included with them in a **main group**, while the element which less closely resembles the corresponding lighter elements is connected with them by a broken line, indicating the smaller similarity. These elements constitute what is called a **sub-group**, denoted in the table by primed numbers. This arrangement of the Periodic System should be studied, the position of the commoner elements in it learned, and the basis of its construction, as indicated by Tables 4 and 5 in the preceding chapter, thoroughly understood.

3. Almost any property of the elements or any class of compounds, if plotted against the atomic numbers, would show a periodicity, as does the number of valence electrons;

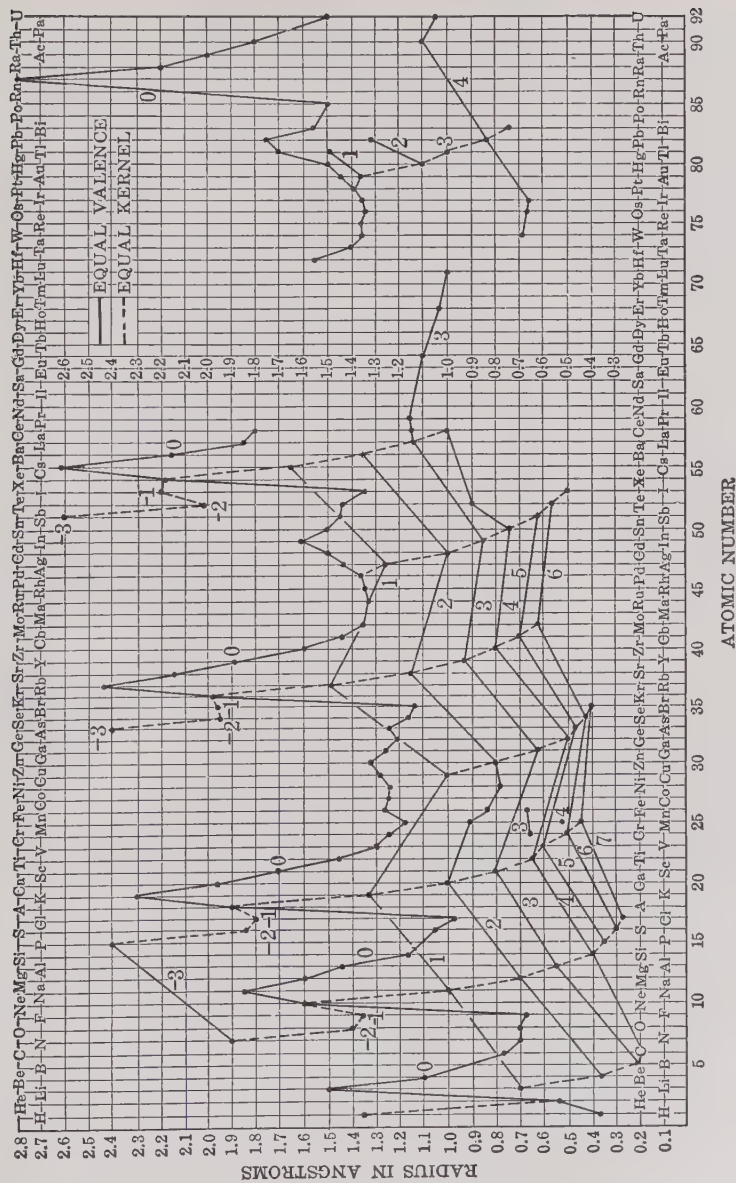


FIG. 1. Atomic and ionic radii.

however, the two most fundamental properties for an understanding of chemical and physical behavior are the size of the atom and the ease of removal of electrons. Accordingly, we have plotted, in Fig. 1, the radii of atoms as they exist in the free elements and in their salts (the radius of the  $\text{Cl}^-$  is assumed to be  $1.81 \times 10^{-8}$  cm.) and, in Fig. 2, the ionizing potentials of the gaseous atoms,

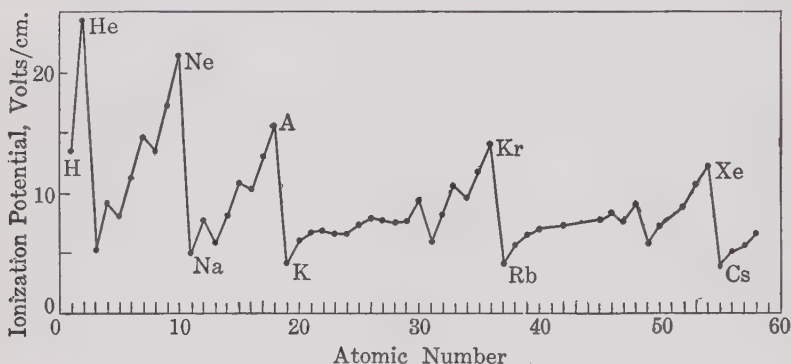


FIG. 2. Ionization potentials of atoms.

*i.e.*, the strength of the electric field in volts per cm. required to detach the first electron from the atom. Let us note particularly several facts revealed by these curves.

4. The radii of the positive kernels decrease regularly in each period for the elements following an alkali metal. This accords with the increasing nuclear charge, which draws closer to itself the electrons in a given energy level. When a new level is begun there is a jump in radius, as seen by the peaks headed by the alkali metal kernels, each higher than the one before. Figure 3 illustrates these relationships by showing the atoms and ions of Li, Be, Na and Mg, drawn to relative scale. This difference also appears in comparing such structures as  $\text{S}^{+6}$ , with two completed electron groups, with  $\text{S}^{--}$ , with three completed groups, the latter of course being much larger.



5. The ionizing potentials of the gaseous atoms, plotted in Fig. 2, are lowest for the largest atoms, as might be expected, since the farther the negative electron is from the positive nucleus the more easily it can be removed. Except for minor fluctuations, the ionizing potential increases along each period, beginning with an alkali metal and ending with a noble gas. It should be noted that the ionizing potentials here plotted are for the first electron only, hence

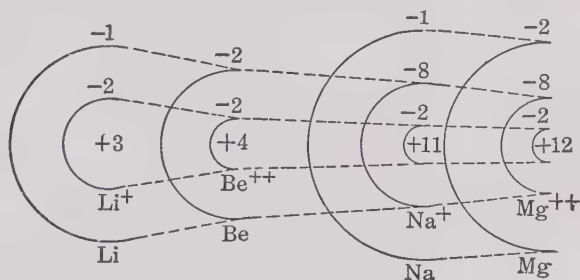


FIG. 3. Relation between size and structure of atoms and ions.

the remainder of the atom does not have the size plotted in the upper portion of the figure except in the cases of the univalent atoms. In harmony with the increase in size the potentials for each period are lower than the corresponding ones of the previous period.

6. **Stability of Compounds.** The rôles of ionizing potential and atomic size in determining chemical stability are indicated by the scheme in Chapter V, Table 1, and we may now correlate the stabilities of compounds with the positions of their elements in the Periodic System. Stability is greater the lower the ionizing potential of the metallic atom and the greater the electron affinity of the non-metallic atom, and both become smaller as we go from the lighter to the heavier members of a main group. On this basis we will expect, for example, KCl to be more stable than NaCl, KCl than KI, CaO than ZnO, H<sub>2</sub>O than H<sub>2</sub>S.

7. Stability is also aided by small size and consequent closeness of approach of the charged atoms, a factor which contributes to the increase in stability in going from iodides to fluorides, but which opposes the effect above noted in going from LiCl to CsCl; indeed it is sufficient to reverse the series in the case of the alkali fluorides, for LiF is the most stable in spite of the larger amount of energy absorbed in changing from Li to  $\text{Li}^+$ .

8. We should note, however, that the type of kernel, as well as its size, is effective in determining this attraction. A striking instance is seen in comparing LiBr with AgBr, where the distances between the charged atoms in the solid are nearly the same, although Ag occupies more space than Li in most of their compounds. We have independent evidence that Ag is able to distort large negative atoms such as Br, and therefore approach closer to them than would otherwise be the case. Another evidence of the superior attractive forces of kernels with approximately 18 electrons is seen in the ability of the ions in the middle of the long periods to form complex ions.

9. The following miscellaneous examples are given as further illustration of the above principles. The stability of hydrogen compounds with negative elements decreases from right to left in the same period, as from HF to  $\text{H}_2\text{O}$  to  $\text{H}_3\text{N}$ , and from HCl to  $\text{H}_2\text{S}$  to  $\text{H}_3\text{P}$ ; it decreases also from the top of a group downwards, as HF to HI,  $\text{H}_2\text{O}$  through  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  to  $\text{H}_2\text{Te}$ , and from  $\text{H}_3\text{N}$  through  $\text{H}_3\text{P}$ ,  $\text{H}_3\text{As}$  to  $\text{H}_3\text{Sb}$ , while  $\text{H}_3\text{Bi}$  is of doubtful existence.

The highest oxidation state of molybdenum is seen in  $\text{MoO}_3$  and  $\text{MoF}_6$  but not in a chloride, the highest being  $\text{MoCl}_5$ . Again, if we compare the compounds of sulfur with bromine, chlorine, oxygen and fluorine, which is the order corresponding to increasing electronegative character, we find that the highest bromide has the formula  $\text{S}_2\text{Br}_2$ ; the highest chloride is  $\text{SCl}_4$ , the highest oxide is  $\text{SO}_3$  but this compound breaks down rather completely above

700° C. into  $\text{SO}_2$  and  $\text{O}_2$ ; and finally the fluoride,  $\text{SF}_6$ , is an exceedingly stable inert substance.

**10. Strength of Acids and Bases.** If we consider a hydroxide as made up of the charged atoms,  $\text{M}^+ \text{O}^{--} \text{H}^+$ , we see that there is a possibility of dissociating, either as a base into  $\text{M}^+$  and  $\text{OH}^-$ , or as an acid into  $\text{MO}^-$  and  $\text{H}^+$ . Which of these takes place and the extent of each is dependent closely upon the relative sizes of the ions involved, although the type of kernel is also significant. The smaller the  $\text{M}^+$  the more closely it is held to the oxygen with a consequent weakening of the attraction between  $\text{O}^{--}$  and  $\text{H}^+$ , hence the less basic and the more acidic is the compound. As illustrations we may note that the hydroxides of the large alkali metal ions are all strong bases, the strength increasing with the size. The same increase in basic strength is shown in descending group 2, but these are smaller ions and weaker bases, the weakest,  $\text{Be}(\text{OH})_2$ , being also weakly acidic, belonging to the transition hydroxides that are amphoteric. The influence of kernel type is seen in the fact that  $\text{Zn}^{+2}$ , with an 18 electron kernel, gives a weaker base, in spite of its larger size, than does the smaller  $\text{Mg}^{+2}$ .

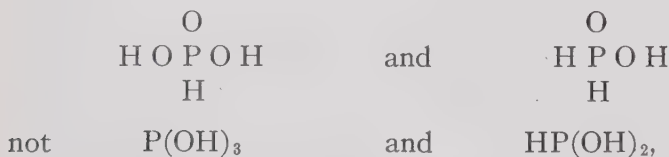
**11.** The more completely the electrons on the atom  $\text{M}$  are removed by surrounding it by oxygen atoms, *i.e.*, the higher its oxidation number, the smaller it is and the more tightly does it hold  $\text{OH}^-$  and the more readily does it allow  $\text{H}^+$  to split off instead. We find, therefore, that sulfuric acid,  $\text{SO}_2(\text{OH})_2$ , is a stronger acid than sulfurous,  $\text{SO}(\text{OH})_2$ ; nitric acid is stronger than nitrous, arsenic than arsenous, etc. Again,  $\text{Mn}^{+2}$  gives a base while  $\text{Mn}^{+7}$  gives an acid;  $\text{Cr}^{+2}$  a base,  $\text{Cr}^{+3}$  an amphoteric hydroxide and  $\text{Cr}^{+6}$  an acid.

**12.** The plot of atomic radii, Fig. 1, serves very well to point out the relation of acid or basic character to the position in the Periodic System. Every positive ion with a radius of less than  $0.5 \times 10^{-8}$  cm. gives an acidic hydrox-

ide, the more so the higher the valence and the higher in the group. Ions slightly exceeding this size may give weak acids in the higher valences, but the ions larger than  $0.9 \times 10^{-8}$  cm. all give bases only. The region of amphoteric behavior, it will be seen, begins with Be in group 2, and runs to Al in group 3, then to group 4 and sub-group 4, with representatives from adjacent groups assisted by variations in valence. In group 5 we start with  $\text{HNO}_3$  and  $\text{HPO}_3$  or  $\text{H}_3\text{PO}_4$ , strong acids, then  $\text{H}_3\text{AsO}_4$ , a weak acid,  $\text{H}_3\text{SbO}_4$ , amphoteric, and hence very weak in both rôles. In the trivalent state we end with  $\text{Bi}(\text{OH})_3$ , a weak base. In group 3 we find  $\text{B}(\text{OH})_3$ , a very weak acid,  $\text{Al}(\text{OH})_3$ , amphoteric, and  $\text{Sc}(\text{OH})_3$ , basic; in group 4 the weak carbonic and silicic acids, titanitic hydroxide, amphoteric, zirconium hydroxide, chiefly basic, and thorium hydroxide, wholly so.

13. Similar trends are evident in the sulfides, where  $\text{As}_2\text{S}_3$  is acidic, dissolving easily in  $\text{S}^{--}$ , while  $\text{Sb}_2\text{S}_3$  dissolves with difficulty and  $\text{Bi}_2\text{S}_3$  not at all. The increase in valence from  $\text{Sb}_2\text{S}_3$  to  $\text{Sb}_2\text{S}_5$  increases the acidic nature sufficiently to allow it to dissolve easily.

14. An apparent exception to this trend exists in the case of the three acids of phosphorus,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_2$ , which do not decrease in strength with diminishing oxygen content. The discrepancy finds its explanation, however, in the fact that part of the hydrogen in  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_2$  is linked, not to oxygen, but to phosphorus. Their structures correspond to



for the former dissociates but two of its three hydrogen atoms and the latter but one.

**15. Oxidation State.** The significance of the octet of valence electrons explains the limiting values for the oxidation states found in the various groups:

Group	0	1	2	3	4	5	6	7	8
Oxidation number	0	+1	+2	+3	+4	+5	+6	+7	+8
					-4	-3	-2	-1	

These limiting values do not always appear in all members of a group, thus no other atom is able to strip 7 electrons from a fluorine atom or 6 from an oxygen atom. The state +8 appears only in  $\text{RuO}_4$ ,  $\text{OsO}_4$ ,  $\text{RuF}_8$ , and  $\text{OsF}_8$ .

Oxidation states lying within these extremes also appear, as illustrated by

	OXIDATION No. OF P		OXIDATION No. OF Cl
$\text{P}_2\text{O}_5$	+5	$\text{KClO}_4$	+7
$\text{P}_2\text{O}_3$	+3	$\text{KClO}_3$	+5
$\text{H}_3\text{PO}_2$	+1	$\text{KClO}_2$	+3
$\text{H}_3\text{P}$	-3	$\text{KClO}$	+1
		$\text{KCl}$	-1

**16.** In the sub-groups numbers corresponding to the group number usually appear, but they are not always the most characteristic, and other states appear which might not be expected on the basis of the Periodic System. The following table illustrates this fact:

	OXIDATION Nos.
Cr	2, 3, 6
Fe	2, 3
Mn	2, 3, 4, 6, 7
Pt	2, 4
Os	2, 4, 8

The horizontal relationships are rather more important than the vertical relationships with these elements, as illustrated by the fact that the oxidation number +2 is char-

acteristic of the successive elements, Cr, Mn, Fe, Co, Ni, Cu, Zn. The oxidation number + 3 is found in the same series from Cr to Co. Again Cu and Ni are more alike than Ni and Pd, or Cu and Ag, and Au is rather more like Pt than Ag.

**17.** It is to be noted that the rare earth elements, which seem to be out of harmony with the rest of the system, all have + 3 as their most characteristic oxidation state.

**18. Solubility of Salts.** The solubility of salts changes in regular order according to the Periodic System in nearly all instances. This is illustrated for a single group, the second, by Table 3.

TABLE 3  
SOLUBILITIES

	HYDROXIDE	SULFATE	CHLORIDE
Magnesium	Insoluble	Soluble	Deliquescent
Calcium	Sparingly soluble	Sparingly soluble	Deliquescent
Strontium	Moderately soluble	Insoluble	Soluble
Barium	Soluble	Very insoluble	Less soluble

**19. Density,** which is mass divided by volume, depends, in the case of solid substances, not only on atomic weight and atomic volume but on the crystal structure and coefficient of expansion as well; hence it is not strange that the density often appears somewhat irregular. Table 4 shows the irregular values for K and Ca which result chiefly from the different rates of increase of atomic weight and atomic volume.

We see, however, the general increase in density in descending a group due to the fact that atomic weight increases faster than atomic size; further, the high densities of the elements in the sub-groups as compared with the main groups resulting from the position of the former in the troughs of the curves of atomic radii.



TABLE 4  
DENSITIES OF SOLID ELEMENTS

GROUP 1	GROUP 2	GROUP 2'	GROUP 1'	GROUP 8'	GROUP 10'
Li 0.53	Be 1.73	Zn 7.1	Cu 8.9	Fe 7.9	Ni 8.7
Na 0.99	Mg 1.74	Cd 8.6	Ag 10.5	Ru 12.0	Pd 11.5
K 0.86	Ca 1.53	Hg 13.5	Au 19.2	Os 22.5	Pt 21.4
Rb 1.52	Sr 2.55				
Cs 1.90	Ba 3.78				

**20. Tensile Strength.** The metals with the greatest tensile strength are found among the sub-groups, starting with 5 and extending to 10. These groups include iron and the metals alloyed with it to make the modern alloy steels, V, Cr, Mo, W, U, Mn and Ni. We may connect high tensile strength with small atomic volume, high melting point and many electron valence shells.

**21. Elements Which Form Complex Ions.** The elements most prone to form complex ions are in the sub-groups and especially in the neighborhood of Group 1' in the second form of the table. Complex ions with ammonia are readily given by the ions of Co, Ni, Cu, Zn, Cd and Ag. Complex cyanides are given by the same elements, also by the platinum metals and iron. Complex chlorides are given chiefly by the platinum metals and gold, as illustrated by  $\text{PtCl}_6^{--}$  and  $\text{AuCl}_4^-$ .

**22. Resemblance between the First Member of a Group and the Second Member of the Succeeding Group.** Some similarity exists between the first element in Groups 1, 2 and 3 and the second element in the succeeding group. Thus lithium, though an alkali metal, resembles magnesium in having a hydroxide and carbonate which are not very soluble, a rather insoluble phosphate and a deliquescent chloride. Beryllium is so much like aluminum that the two elements are difficult to separate. Boron is like silicon in physical properties and gives compounds similar in many respects. The borates of all but the alkali metals, like the corresponding silicates, are insoluble in water, and when fused tend to give glasses on cooling.

**23. Radioactive Elements.** As might be expected, it is the heaviest and most complex atoms which tend to break down into simpler ones, and all of the elements of higher atomic weight than bismuth are radioactive. These are, accordingly, found at the bottom of the table. The odd-numbered elements are, in general, less stable than the even-numbered ones, as shown by their relative abundance and by their life periods.

**24. Prediction of Unknown Elements.** The value of the Periodic System was demonstrated in very striking fashion by the prediction of unknown elements by Mendeléeff. At the time he constructed his table it was obvious that several gaps should be left in order to have the succeeding elements fall into their proper groups. Such gaps were to be found at the places now filled by scandium, gallium and germanium. From the properties of the adjacent elements, Mendeléeff predicted the properties of the unknown elements. The remarkable accuracy of these predictions is illustrated by the following comparison of the unknown element called by Mendeléeff "ekasilicon," with germanium, discovered later by Winkler.

EKASILICON	GERMANIUM
At. wt. 72, density 5.5.	At. wt. 72.5, density 5.46.
Oxide $\text{EsO}_2$ , density 4.7.	Oxide $\text{GeO}_2$ , density 4.7.
Chloride $\text{EsCl}_4$ , liquid, boiling slightly below $100^\circ$ , density 1.9.	Chloride $\text{GeCl}_4$ , liquid, boiling at $86^\circ$ , density 1.887.
Ethide, $\text{Es}(\text{C}_2\text{H}_5)_4$ , liquid, boiling at $160^\circ$ , density 0.96.	Ethide, $\text{Ge}(\text{C}_2\text{H}_5)_4$ , liquid, boiling at $160^\circ$ , density slightly less than 1.
Fluoride, $\text{EsF}_4$ , not gaseous.	Fluoride, $\text{GeF}_4$ , white, solid.

The foregoing comparison should serve as an illustration of the value of the Periodic System to the student of chemistry, for if an undiscovered element can be foretold so brilliantly by its aid, then any knowledge a student may

have of some elements may be similarly projected to deduce the properties of adjacent elements. The use of the Periodic System, therefore, enormously increases the effectiveness of a given amount of mental effort, and it is very important to form the habit of using it constantly.

### EXERCISES

1. In what regions of the Periodic System will elements be found which have the following characteristics most strongly marked: tendency to form stable compounds with hydrogen, tendency to form ammonia complex ions, tendency to form strongest oxygen acids, radioactivity, maximum positive valence, lowest melting point, maximum negative valence, the strongest reducing power, amphoteric nature of the hydroxides, the greatest tensile strength?

2. Arrange the following elements in their proper order in groups 1 and 2 of the Periodic System: Li, Mg, Ba, Ca, K, Na, Cs, Be, Rb.

3.  $\text{BaCl}_2$  is moderately soluble,  $\text{CaCl}_2$  is deliquescent; what can you conclude regarding  $\text{RaCl}_2$ ? How would you expect the solubilities of  $\text{LiCl}$  and  $\text{NaCl}$  to compare?

4. How do each of the following properties vary from left to right in the same row of the Periodic System: (a) the basic character of the hydroxide, (b) the melting point, (c) the positive valence, (d) the electrical resistance of the element?

5. Discuss the trend of properties of the elements of group 2 and their compounds as you descend the group.

6. Compare the salt-like characters of binary compounds with the positions of their constituents in the Periodic System.

7. From the place of Cd in the Periodic System, what deduction would you make regarding: (a) the melting point of the metal; (b) the solubility of its sulfate; (c) the ionization of its chloride?

8. Compare the strength as acids of (a)  $\text{H}_3\text{AsO}_3$  and  $\text{H}_3\text{SbO}_3$ , (b)  $\text{H}_3\text{AsO}_3$  and  $\text{H}_3\text{AsO}_4$ . Justify your answers by either experimental facts known to you, or by theoretical considerations, or by valid analogies.

9. How do the differences between  $\text{H}_3\text{AlO}_3$  and  $\text{H}_3\text{BO}_3$  agree with the places of Al and B in the Periodic System?

10. Explain on theoretical grounds which you would expect to be more hydrolyzed, (a)  $\text{NaNO}_2$  or  $\text{NaAsO}_2$ ; (b)  $\text{Na}_2\text{SO}_3$  or  $\text{Na}_2\text{TeO}_3$ ?

11. (a) Name the halogens in their order. (b) Which one has the greatest tendency to take on electrons? (c) Which has the highest melting point? (d) Which is the weakest oxidizing agent?

12. From the position of beryllium in the Periodic System, deduce (a) whether  $\text{Be}(\text{OH})_2$  or  $\text{Mg}(\text{OH})_2$  is the stronger base; (b) whether  $\text{BeS}$

could be precipitated with  $\text{H}_2\text{S}$ ; (c) whether  $\text{BeSO}_4$ , or  $\text{MgSO}_4$  is more soluble; (d) whether Be or Mg evolves more heat upon reaction with chlorine.

13. Explain on a theoretical basis which of the 2 elements, Ti or Th, would (a) more likely form a compound with hydrogen; (b) be the better conductor of electricity; (c) be more easily reduced from its dioxide; (d) give the more basic hydroxide; (e) give a more completely hydrolyzable chloride.

14. Classify the following compounds according to the valence of the phosphorus they contain: (a)  $\text{P}_2\text{O}_5$ ; (b)  $\text{PCl}_3$ ; (c)  $\text{PH}_3$ ; (d)  $\text{H}_3\text{PO}_2$ ; (e)  $\text{H}_4\text{P}_2\text{O}_7$ ; (f)  $\text{HPO}_3$ ; (g)  $\text{NaPO}_2$ ; (h)  $\text{PbHPO}_4$ ; (i)  $\text{PCl}_5$ ; (j)  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ .

15. Deduce from their positions in the Periodic System whether (a) Os or Ir should show the higher valence; (b)  $\text{Rh}^{++}$  or  $\text{Pd}^{++}$  should give the more stable complex with  $\text{NH}_3$ ; (c) Ni or Co should be the better catalyst for reactions involving  $\text{H}_2$ ; (d)  $\text{Ni}(\text{OH})_2$  or  $\text{Co}(\text{OH})_2$  should be the stronger base.

16. Compare the stabilities of the trichlorides of the elements in Group 5 and justify your comparison upon theoretical grounds.

17. State 5 chemical or physical characteristics of the element below iodine in Group 7.

18. Which would you expect to be the stronger reducing agent, (a)  $\text{Fe}^{++}$  or  $\text{Co}^{++}$ ; (b)  $\text{H}_2\text{S}$  or  $\text{H}_2\text{Te}$ ? Explain your answer very briefly.

19. Which would you expect to be the stronger oxidizing agent,  $\text{Ni}(\text{OH})_2$  or  $\text{Fe}(\text{OH})_2$ ? Give the basis for your answer.

20. Deduce from the positions in the Periodic System of Ni and Co (a) whether  $\text{Ni}^{++}$  or  $\text{Co}^{++}$  is the stronger reducing agent; (b) whether  $\text{Ni}(\text{OH})_2$  or  $\text{Co}(\text{OH})_2$  is more easily soluble in  $\text{NH}_4\text{OH}$ ; (c) which element is harder; (d) which has the higher melting point; (e) whether  $\text{CoS}$  or  $\text{NiS}$  is more soluble in water.

21. From your knowledge of the properties of  $\text{Fe}^{++}$  and  $\text{Cu}^{++}$ , compare (a) the solubility of  $\text{NiS}$  and  $\text{CuS}$ , (b) the stability of the ammonia complexes of  $\text{Ni}^{++}$  and  $\text{Cu}^{++}$ , (c) the oxidizing power of  $\text{Fe}(\text{OH})_3$  and  $\text{Ni}(\text{OH})_3$ .

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# Chapter XVIII

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## *Molecular Structure*

### A. CARBON COMPOUNDS

1. An understanding of molecular structure was first obtained in connection with the compounds of carbon. Both plants and animals are made up chiefly of carbon compounds, from which it is evident that nature has prepared an enormous variety of them. It used to be thought that such compounds could be synthesized only through the aid of living matter, whence they were called **organic** compounds. Although we have since learned that no such limitation exists, we still designate the chemistry of the carbon compounds as **organic chemistry**, and find it advantageous, on account of its peculiarities, to treat it as a very distinct branch of chemistry. The labors of chemists have added greatly to the number of carbon compounds until today there are known over 200,000 of them. The majority contain only carbon, hydrogen, oxygen and nitrogen. Now the simple determination of the number of atoms of each kind in the molecule does not suffice to identify the substance, or to suggest methods for its preparation, any more than given amounts of lumber, nails, bricks, mortar, etc., would serve to identify a house. Indeed there are many instances where several substances contain atoms of the same kind and number. For example, there are two substances having the formula  $C_2H_6O$ : one is ordinary alcohol, a liquid with a boiling point of  $78^\circ$  and a density of 0.789 at  $20^\circ$ ; the other

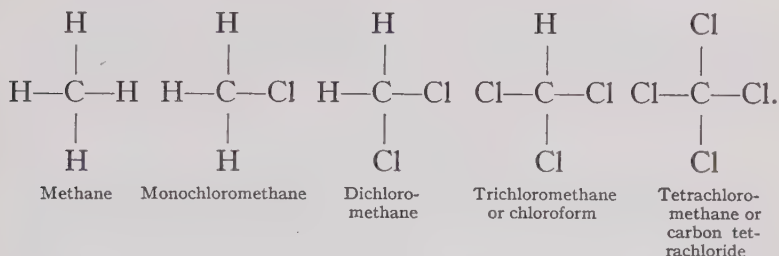
is dimethyl ether, a gas which becomes liquid at  $-23.6^{\circ}$  under 1 atmosphere pressure, and which has a different odor and generally different properties. Taking a more complex formula such as  $C_6H_{12}O_6$ , we find a much larger number of corresponding substances, in this case not less than 64. Such substances are called **isomers**. The differences in their properties can, of course, be due only to differences in arrangement of the atoms within the several molecules. The determination of this arrangement has therefore been a fundamental task in the study of carbon compounds.

2. The nature of the evidence used in the determination of the structure of these molecules is not difficult to comprehend. The first principle used is that the co-valence of carbon is four. It is rarely if ever necessary to assume that any carbon atom is surrounded by more than four other atoms. It makes little or no difference whether the combining atoms have a positive or a negative valence. Thus we may start with  $CH_4$ , which is known as methane or marsh gas, and is a prominent constituent of natural gas, and in which we might be inclined to say that the carbon is negative, and we can change progressively, by the successive substitution of chlorine for hydrogen, to  $CH_3Cl$ ,  $CH_2Cl_2$ ,  $CHCl_3$ , which is chloroform, and finally  $CCl_4$  (used in fire extinguishers and in cleaning). In this last we would doubtless conclude that the carbon is positive, but in the intermediate compounds we see that the question of sign becomes rather confusing. Since we usually consider hydrogen positive and chlorine negative, we might assume the charges on the carbon to be  $-2$  in  $CH_3Cl$ ,  $-0$  in  $CH_2Cl_2$  and  $+2$  in  $CHCl_3$ , that is, different in all five cases. However, we note that in all of them the carbon remains attached to four other atoms, without regard to sign.

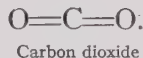
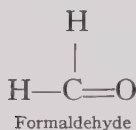
The organic chemist takes as fundamental the existence of four "bonds" for every carbon atom. Each bond is



usually indicated by a simple dash, thus the four compounds given above are usually written as follows:

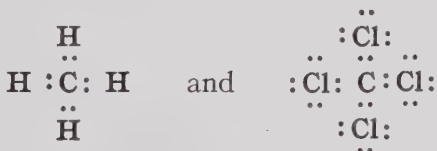


If a "bivalent" element is combined with carbon it is assumed that two of the bonds of carbon are required, thus forming a "double bond," in harmony with the fact that a carbon atom can hold but two atoms of oxygen, as shown by the following formulas:

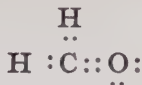


Other examples of formulas written upon this basis will be found later in this chapter.

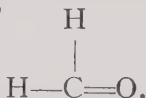
**3. The Electron-Pair Bond.** The reason for the four bonds per carbon atom is seen in the four valence electrons, each forming a pair with an unpaired electron from another atom. The hydrogen atom, H, and the chlorine atom,  $\cdot\ddot{\text{Cl}}\cdot$ , alike have one such electron and can form not only



but the intermediate compounds as well. An oxygen atom, O, can take up 2 of the electrons of a carbon atom, leaving the other two free to unite, say, with hydrogen, giving

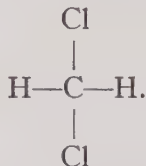
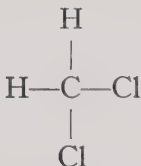


which would be written ordinarily with a "double bond" between C and O, thus,



Such bonds may, it is true, be more or less polar, the bonding electrons in  $\text{CH}_4$  being shifted somewhat towards the carbon and in  $\text{CCl}_4$  more or less towards the chlorine.

**4. Arrangement of Atoms about the Carbon Atom.** If the atoms about the carbon atom in such a compound as  $\text{CH}_2\text{Cl}_2$  were all in the same plane, there would be a possibility of two arrangements which might give rise to isomers having somewhat different properties, as follows:



In one case the like atoms are adjacent, in the other they are opposite. The fact is, however, that neither in this case,

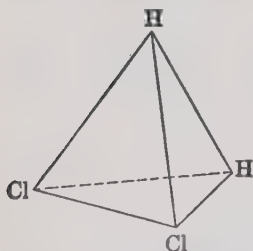


FIG. 1. Tetrahedral arrangement about a carbon atom.

nor yet when any other atoms or groups have been substituted for the hydrogen and chlorine respectively, has it been possible to prepare different isomers. However, if the surrounding atoms or radicals are arranged in tetrahedral form about the central atom, as shown in Fig. 1,

there can be only one arrangement, for each corner of a tetrahedron is adjacent to every other. The non-existence of such isomers, therefore, is evidence for the tetrahedral arrangement.

This tetrahedral arrangement again corresponds to the nature of the isomers found in cases where the central carbon atom is surrounded by four different atoms or groups. Figure 2 shows two arrangements which are different in the sense that the right and left hands are different, or right and left handed screws are different. In each case, one is the mirror image of the other. There exist great numbers of such isomers, alike in all ordinary properties, just as right and left handed screws may be identical in weight, form, etc., but which show a remarkable difference in optical

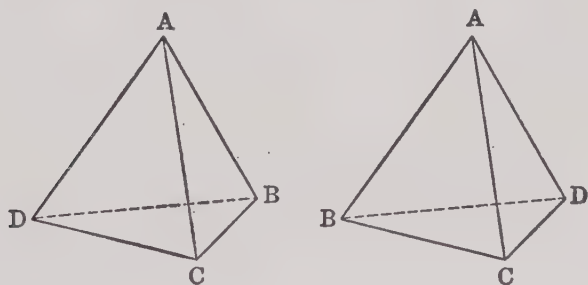
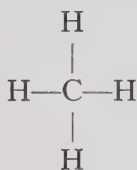


FIG. 2. Optical isomerism.

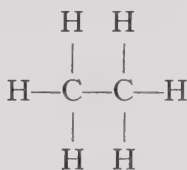
behavior. Light which is made to vibrate all in one plane, or polarized, when passing through one of these isomers will be rotated to the right, and through the other an equal amount to the left, just as right and left handed screws would be rotated equally in opposite directions in advancing a given distance. This behavior is thus consistent with the tetrahedral structure.

We have, therefore, very good evidence that the atoms about a carbon atom are arranged approximately in tetrahedral manner. The representation of this upon paper is not very satisfactory since it requires the use of perspective, but since optical isomers are possible only when the four surrounding atoms or groups are different, it suffices for most compounds to use the plane arrangement.

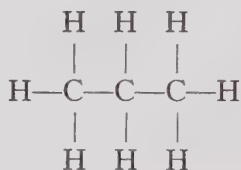
**5. Paraffin Series.** The immense number of carbon compounds is chiefly due to the ability of carbon atoms to link to each other indefinitely. The simple linear arrangement of the carbon atoms gives rise to the **paraffin series** of hydrocarbons. The following structural formulas show the first few members of the series. This type of molecule can evidently be extended indefinitely, for the substance  $C_{60}H_{122}$  has been prepared. The series can obviously be represented by the general formula  $C_nH_{2n+2}$ .



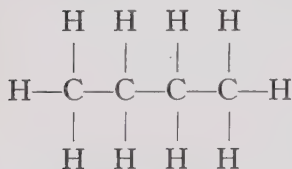
Methane



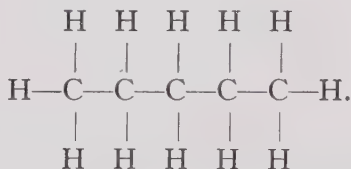
Ethane



Propane



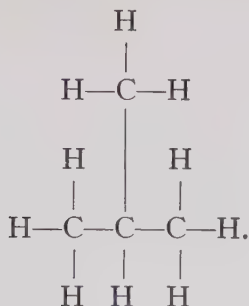
Butane



Pentane

The characteristics of the series are indicated in Table 1, containing selected members. Its members are constituents of paraffin petroleum and the neighboring members come over together as the petroleum is distilled. The gaseous members are contained in natural gas, the low boiling liquids are in gasoline, and as the boiling points rise we find the substances successively in "distillate," kerosene, "light" and "heavy" lubricating oils. When the melting points enter the range of ordinary temperatures we get vaseline, then soft paraffin, and then hard paraffin.

Beginning with butane, isomers are possible. Thus we may have, in addition to the straight chain, an arrangement with a side chain, as follows, called iso-butane.



This has somewhat different properties, *e.g.*, a boiling point of  $-17^\circ$ , whereas normal butane boils at  $+1^\circ$ . With pentane there are two additional isomers, and the number rapidly increases with increasing molecular complexity.

TABLE 1  
PARAFFIN SERIES OF HYDROCARBONS

FORMULA	NAME	MELTING POINT	BOILING POINT	DENSITY
$\text{CH}_4$	Methane	$-184^\circ$	$-161^\circ$	
$\text{C}_2\text{H}_6$	Ethane	$-172^\circ$	$-88^\circ$	
$\text{C}_3\text{H}_8$	Propane	$-190^\circ$	$-45^\circ$	
$\text{C}_4\text{H}_{10}$	Butane	$-135^\circ$	$+1^\circ$	
$\text{C}_5\text{H}_{12}$	Pentane	$-131^\circ$	$+36^\circ$	
$\text{C}_6\text{H}_{14}$	Hexane	$-94^\circ$	$69^\circ$	
$\text{C}_7\text{H}_{16}$	Heptane	$-90^\circ$	$98^\circ$	.700
$\text{C}_8\text{H}_{18}$	Octane	$-57^\circ$	$125^\circ$	.718
$\text{C}_9\text{H}_{20}$	Nonane	$-51^\circ$	$150^\circ$	.733
$\text{C}_{10}\text{H}_{22}$	Decane	$-32^\circ$	$174^\circ$	.745
$\text{C}_{11}\text{H}_{24}$	Undecane	$-27^\circ$	$197^\circ$	.774
$\text{C}_{12}\text{H}_{26}$	Dodecane	$-12^\circ$	$216^\circ$	.773
$\text{C}_{13}\text{H}_{28}$	Tridecane	$-6^\circ$	$234^\circ$	.775
$\text{C}_{14}\text{H}_{30}$	Tetradecane	$+6^\circ$	$252^\circ$	.775
$\text{C}_{24}\text{H}_{50}$	Tetracosane	$+51^\circ$	$243^\circ$	.779
$\text{C}_{35}\text{H}_{72}$	Pentatriacontane	$+75^\circ$	$331^\circ$	.782
$\text{C}_{60}\text{H}_{122}$	Dimyricyl	$+102^\circ$	—	—

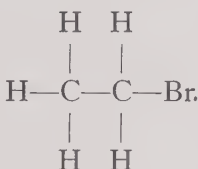
At 15 mm.  
pressure

At  $0^\circ$   
point

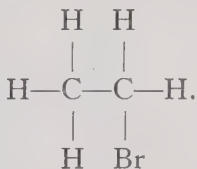
6. To justify these structures we must introduce a **second principle** used in determining molecular constitution of carbon compounds. This asserts that **in organic reactions ordinarily the smallest possible number of bonds are**

**broken.** Organic reactions are characterized by a much greater slowness than most inorganic reactions. It is often necessary to heat the reacting substances together for hours. This inertness makes it possible to disturb only a part of the molecule, so that a certain group, or "radical," known to be present in the molecule before the reaction, is likely to remain intact in some product of the reaction.

7. Let us illustrate this principle. Ethane can have only the structure already assigned, in view of the valences. By allowing bromine to act upon ethane in the presence of light it is possible to replace hydrogen by bromine and to prepare monobromethane,  $C_2H_6 + Br_2 = C_2H_5Br + HBr$ . This can hardly have any other than the ethane structure,



(Remember that all of the carbon bonds are alike, in view of their tetrahedral arrangement, so that the formula just written is identical with the following, which only appears to be different because they are written in one plane.)

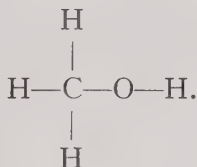


Now if this bromide is treated with zinc, we get zinc bromide and butane, the isomer boiling at  $+1^\circ$ . It seems that the bromine has been removed and the remainders of the two molecules have joined together without further alteration. (This remainder,  $C_2H_5$ , is called the **ethyl radical**.) To consider this isomer as isobutane would ob-

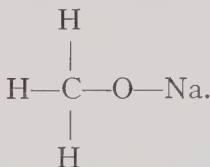


vously require us to assume that the reaction involved a much more complicated and hence far more improbable breaking and rejoining of bonds. Isobutane must be prepared in a very different way.

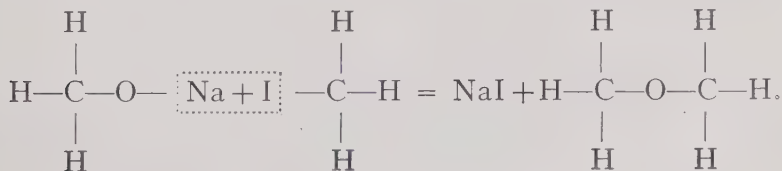
8. As a further example of the application of this principle to the determination of structure, let us consider the isomers first mentioned, ethyl alcohol and dimethyl ether, both  $C_2H_6O$ . Starting with the methane structure, we will consider  $CH_3-$  to be the **methyl radical**, which would be left by the removal of one atom of hydrogen. Methyl iodide (or moniodomethane) when treated with a solution of KOH gives methyl hydroxide (methyl alcohol, "wood alcohol"),



(Additional evidence for this structure will be given later.) Treatment with sodium replaces *one* hydrogen atom, giving

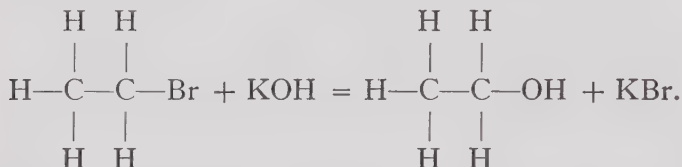


If this is allowed to react with methyl iodide, sodium iodide is produced, and the simplest possible way for the remainders of the 2 molecules to react is simply to join together, with an oxygen atom linking 2 methyl groups.



This is the gaseous isomer, and is called dimethyl oxide, or dimethyl ether.

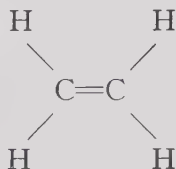
The structure of the other isomer is indicated by the fact that it is easily derived from ethyl bromide by the action of a solution of KOH.



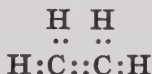
This isomer, therefore, appears to be ethyl hydroxide in structure. To assume that this reaction involves breaking the bond between the carbon atoms to give dimethyl ether would appear highly improbable, just as it would be to assume that the previous reaction would directly link the carbon atoms.

It is usually possible to prepare a given compound from more than one source, or to decompose it in more than one way. Where the same structural formula can account for all known reactions it naturally inspires a high degree of confidence. There are, however, cases where extensive rearrangements evidently take place during certain reactions. The determination of structure in such cases has often proven very difficult, and the history of organic chemistry is not without its sharp controversies.

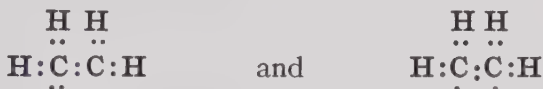
**9. Unsaturated Hydrocarbons.** There are a number of hydrocarbons which contain less than the maximum amount of hydrogen. Thus ethane is  $\text{C}_2\text{H}_6$ , while **ethylene** is  $\text{C}_2\text{H}_4$ . The unused carbon bonds are commonly supposed to be joined together, thus



giving a double bond. This corresponds to a bond of 4 electrons instead of 2, and may be represented



The four electrons of the double bond are, of course, not stationary, and their motion, through different positions, called resonance, may lead to a variety of instantaneous configurations, including not only the above but also



Such resonance may allow a compound to react in a way favored by one of these configurations even though the molecule spends but a small portion of the time therein.

The double bond is more or less readily "broken" by the addition of other atoms giving "saturated" compounds. Ethylene may be made to add more hydrogen, becoming ethane.

10. Still more hydrogen may be lacking, giving acetylene,  $\text{C}_2\text{H}_2$ , usually prepared by the action of water on calcium carbide,



The acetylene molecule requires the assumption of a **triple bond**, if the quadrivalence of carbon is to be maintained, and is written



Hydrocarbons with longer chains may have double or triple bonds occurring anywhere in the chain, such as

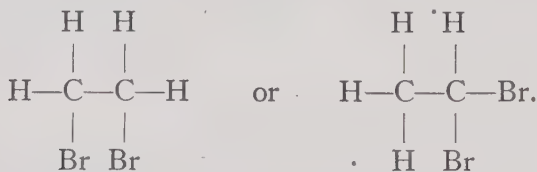


11. **Derivatives of the Paraffin Series.** A hydrogen atom in a paraffin hydrocarbon may be replaced by another atom

or radical giving different series of derived substances. The nomenclature of most of these is based upon the name of the univalent radical that would be left upon the hypothetical removal of an atom of hydrogen. The first eight of these radicals are as follows:  $\text{CH}_3$ — **methyl**;  $\text{C}_2\text{H}_5$ — **ethyl**;  $\text{C}_3\text{H}_7$ — **propyl**;  $\text{C}_4\text{H}_9$ — **butyl**;  $\text{C}_5\text{H}_{11}$ — **amyl**;  $\text{C}_6\text{H}_{13}$ — **hexyl**;  $\text{C}_7\text{H}_{15}$ — **heptyl**;  $\text{C}_8\text{H}_{17}$ — **octyl**. It will be seen that the names of all but the fifth are derived from those of the corresponding hydrocarbons. The radical  $\text{C}_5\text{H}_{11}$ — might be called pentyl, but is called amyl instead.

The name of the derivative is thus simply derived in most cases from that of the radical: for example,  $\text{C}_2\text{H}_5\text{Cl}$  is ethyl chloride;  $\text{C}_4\text{H}_9\text{I}$  is butyl iodide;  $\text{CH}_3\text{—O—CH}_3$  is dimethyl oxide, or, since such oxides are called ethers, dimethyl ether;  $\text{C}_2\text{H}_5\text{—O—C}_3\text{H}_7$  is ethyl-propyl ether;  $\text{C}_2\text{H}_5\text{NO}_3$  is ethyl nitrate. Other examples will appear in the following paragraphs.

**12. Halogen Derivatives.** Chlorine and bromine react directly with the hydrocarbons, replacing one or more hydrogen atoms. Iodine is substituted by way of other derivatives, for example,  $\text{CH}_3\text{OH} + \text{HI} = \text{CH}_3\text{I} + \text{H}_2\text{O}$ . A few examples of such derivatives have already been given. Other structures can be written *ad libitum* from the principles already given. Isomerism is encountered even in such a simple derivative as  $\text{C}_2\text{H}_4\text{Br}_2$ , which can be either



The first is got by adding bromine to ethylene, and is therefore called ethylene bromide, while the second is called ethylidene bromide. (Both are dibromoethanes.)

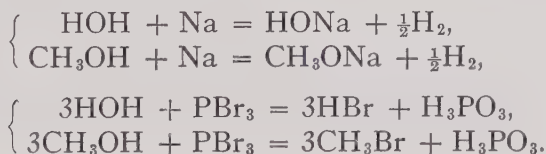
**13. Alcohols.** The hydroxides of the paraffin radicals are the alcohols. In fact, the name alcohol has caused the

radicals of the paraffin series to be called the **alkyl** radicals. If we represent such a radical by the symbol, Alk, we can express the general formula of an alcohol by the formula, AlkOH. The first member of the series is  $\text{CH}_3\text{OH}$ , called methyl alcohol or methanol. (This latter name is preferable, because it avoids the suggestion of beverage use, which is very dangerous.) It is one product of the destructive distillation of wood, hence the name "wood alcohol."

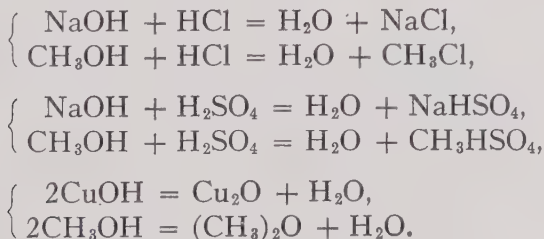
The second member is  $\text{C}_2\text{H}_5\text{OH}$ , ethyl alcohol or ethanol. This is the alcohol chiefly produced in fermentation. The layman usually thinks of it as the important constituent of various beverages, which he regards as a blessing or a curse, according to his point of view, but he rarely realizes that it plays an exceedingly important part in chemical industry.

**14.** We may introduce in this connection a **third principle** which aids in determining molecular constitution, which is that **substances which have similar constitution show similar behavior.**

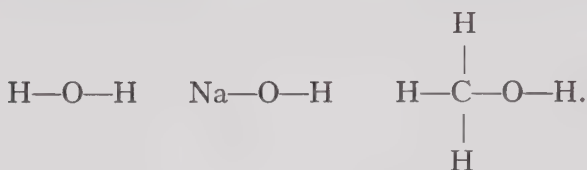
Water may be regarded as hydrogen hydroxide, and methyl alcohol as methyl hydroxide, and this corresponds to the similarity of certain of their reactions, for example,



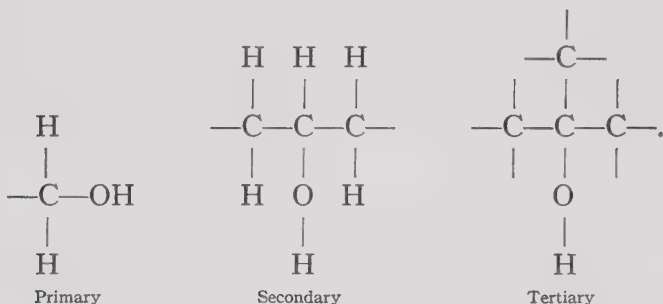
Again, the alcohols act similarly to bases in some of their reactions, as shown by the equations



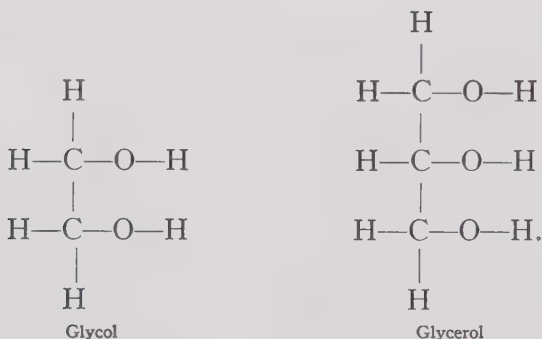
The graphic formulas of the alcohols should, therefore, be related to those of water and bases in being hydroxides.



Alcohols are divided into three classes, according to the number of carbon atoms linked to the one bearing the hydroxyl. The three structures are:



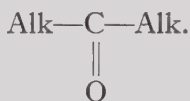
The vacant bonds may be occupied by either hydrogen or further carbon atoms. There are also alcohols containing more than one hydroxyl. We will mention only two, glycol, and glycerol or glycerin.



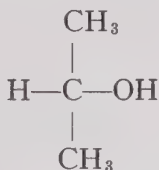


**15. Ethers.** When alcohols are distilled with sulfuric acid water is removed and alkyl oxides, called ethers, are produced, as illustrated by the preceding reaction. The most important is diethyl ether, used extensively as an an-aesthetic. The general formula of an ether is  $\text{Alk}-\text{O}-\text{Alk}$ . The two alkyl groups need not be the same.

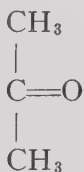
**16. Ketones.** The primary, secondary, and tertiary alcohols behave differently upon oxidation. The tertiary are split up into simpler products. The secondary are changed to ketones, whose general formula is



Thus secondary propyl alcohol,

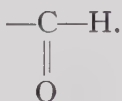


would give dimethyl ketone,

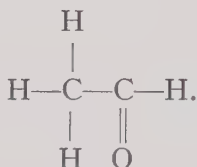


commonly called acetone, a liquid much used as a solvent for varnishes, etc.

**17. Aldehydes.** The primary alcohols upon mild oxidation give first aldehydes, characterized by the group

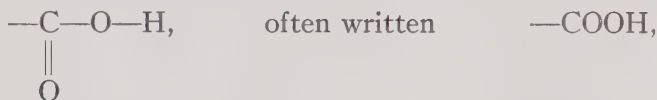


The simplest aldehyde is  $\text{H}_2\text{CO}$ , formaldehyde, made by passing air and vapors of methyl alcohol over a glowing platinum catalyst. It is a gas, soluble in water or alcohol, and is much used as a disinfectant. The second is acetaldehyde,

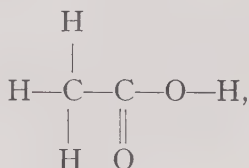


The next would have ethyl in place of methyl, and so on.

**18. Acids.** The further oxidation of the aldehyde group gives the **carboxyl** group,

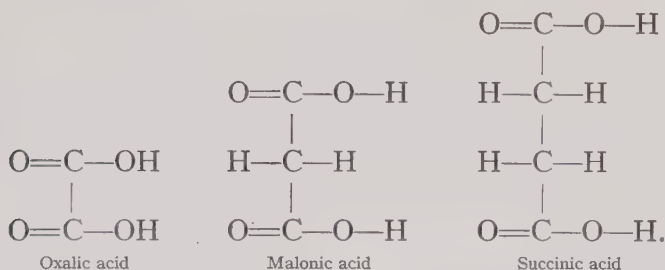


characteristic of organic acids. Ethyl alcohol thus finally becomes acetic acid,

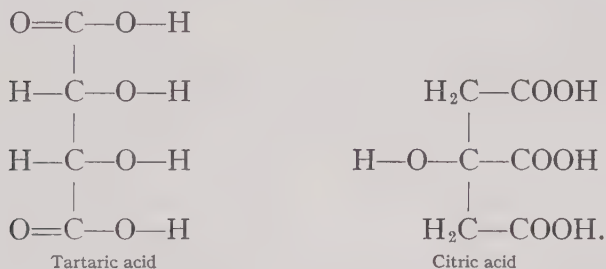


in the process of forming vinegar. The acids of the paraffin series include many important substances. The following are the names corresponding to the number of carbon atoms present: 1, formic; 2, acetic; 3, propionic; 4, butyric (the acid responsible for the odor of rancid butter); 5, valeric; 16, palmitic; 18, stearic. We may mention also oleic acid, which differs from stearic in having a double bond between two of its carbon atoms. The sodium salts of these last three acids are present in ordinary soaps.

There are other acids containing more than one carboxyl group, such as

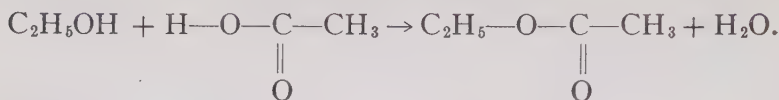


There are others containing both carboxyl and hydroxyl groups, such as tartaric acid, one of the acids of grapes, and citric acid, the acid of lemons and oranges.



The two middle carbon atoms of tartaric acid are joined each to four different atoms or groups, so that optical isomers are possible. The construction of tetrahedral models is necessary to make this altogether clear. Citric acid has no asymmetric carbon atom.

**19. Esters.** We have seen that the alcohols are hydroxides, analogous to bases, and that they react with acids (slowly) with elimination of water (which is usually removed by mixing with sulfuric acid) to form substances analogous to salts; these are called esters. We may have esters of either inorganic or organic acids. We have already given examples of the former. The latter may be illustrated as follows:



Ethyl alcohol

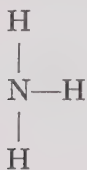
Acetic acid

Ethyl acetate

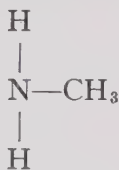
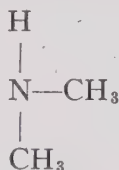
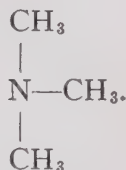
The esters of the organic acids are pleasant smelling liquids, many of which are used in artificial flavorings.

Glycerol forms important esters. Its trinitrate is commonly called nitroglycerin, which is a constituent of dynamite and of smokeless powders. Its esters with the higher paraffin acids are the fats. Glyceryl tripalmitate is palmitin, the chief constituent of palm oil; glyceryl tristearate is stearin, the chief constituent of beef tallow; glyceryl trioleate is olein, found in olive oil, lard, etc. Most fats and oils of animal or vegetable origin contain varying amounts of these esters.

**20. Amines.** The substitution of the hydrogen atoms of ammonia by alkyl radicals gives amines.



Ammonia

Methylamine  
A primary amineDimethylamine  
A secondary amineTrimethylamine  
A tertiary amine

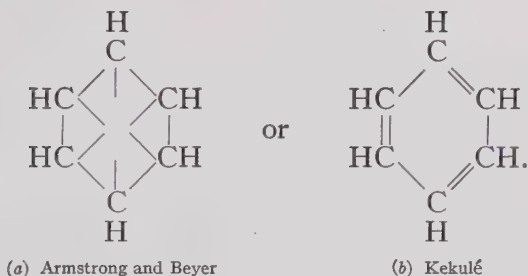
The amines obey the rule regarding the parallelism of properties and structure in that they are chemically like ammonia.

**21.** The combination of  $-\text{NH}_2$  and  $-\text{COOH}$  in the same molecule gives an **amino-acid**. These are peculiar in having both a basic and an acidic group; hence both are weak, and there is the possibility of self-neutralization. These acids can combine with each other indefinitely to form the proteins, essential constituents of our food, and the basic material of living organisms.

**22. Cyclic Compounds.** In all of the preceding compounds we have straight or branching chains of carbon

atoms. There is another important class of organic compounds in which the carbon atoms are joined to form closed rings. They are called cyclic or **aromatic** compounds, to distinguish them from the straight chain or **aliphatic** compounds.

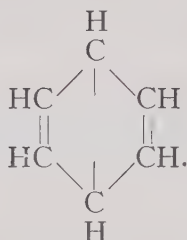
The most important aromatic compound is **benzene**,  $C_6H_6$ , in which the carbon atoms form a ring with a hydrogen atom on each,



**23. Resonance in the Benzene Molecule.** What to do about the fourth carbon bond has always been something of a problem, for the organic chemist does not like to abandon the quadrivalence of carbon, in spite of the extraordinary stability of benzene. Indeed, the extra bond can be called into play, strong reduction adding six more hydrogen atoms. Kekulé drew alternating double and single bonds, as shown at (b), but benzene does not show the ordinary reactions of the double bond, such as the addition of bromine. If the carbon bonds are represented in tetrahedral form, it is possible to construct a very compact structure corresponding to the first formula.

It seems probable that the extra electrons or bonds in the benzene molecule are not permanently in any one position, such as those represented by the above two formulas, but are moving about with great rapidity from one extreme Kekulé formula to the other, with the double bonds in the alternate positions, with the Armstrong and Beyer position

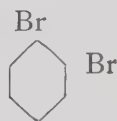
traversed on the way. There is reason to believe that still another position is involved, represented by



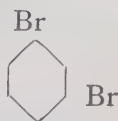
In representing the benzene ring for ordinary purposes we usually ignore the above complexities and write a simple hexagon, with hydrogen understood at the corners unless occupied by some other element or radical.

Evidence for the ring structure is found, first, in the fact that when one hydrogen atom is substituted by something else, say bromine, giving monobromobenzene, there are no isomers. On the other hand, if bromine is substituted in the corresponding open chain, such as hexane, three isomers are possible, depending upon whether the bromine is on the end carbon, next to the end, or the third from the end.

Additional evidence is furnished by the number of di-substitution products. There are three dibromobenzenes, corresponding to the three following arrangements:



Ortho-



Meta-



Para-

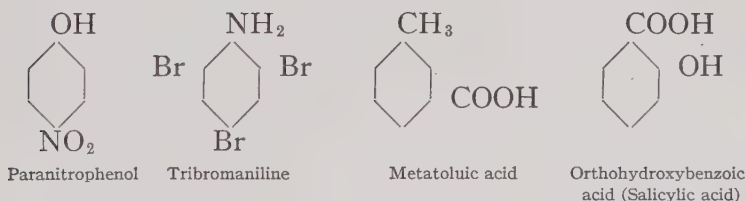
Which of the three substances actually corresponds to each arrangement is readily determined by substituting a third hydrogen atom, when the orthodibromobenzene can give two isomeric tribromobenzenes, the meta three and the para only one.



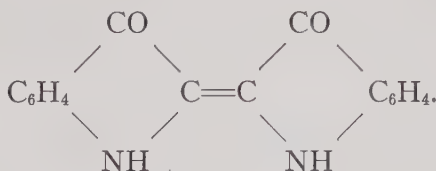
**24. Benzene Derivatives.** If we designate the benzene ring minus one of its hydrogen atoms as the **phenyl** radical by the symbol  $\phi$ , then we can represent very simply a few of the important derivatives as follows:

$\phi$ OH	Phenol (carbolic acid)
$\phi$ COOH	Benzoic acid
$\phi$ CH <sub>3</sub>	Toluene
$\phi$ NH <sub>2</sub>	Aniline
$\phi$ NO <sub>2</sub>	Nitrobenzene
$\phi$ CH <sub>2</sub> OH	Benzyl alcohol
$\phi$ CHO	Benzaldehyde
$\phi$ CO · CH <sub>3</sub>	Phenyl methyl ketone
$\phi$ —N=N— $\phi$	Azobenzene
$\phi$ — $\phi$	Diphenyl

Further substitutions may be made, as in



The artificial dyestuffs are rather complicated molecules, most of which contain one or more benzene rings. One of the simplest is indigo,



There are other substances containing several benzene rings linked together, illustrated by the following:



Naphthalene



Anthracene

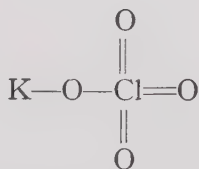
## B. INORGANIC COMPOUNDS

The determination of molecular structure in the case of inorganic compounds is a less urgent question because of the almost complete absence of isomers which would require for their explanation a knowledge of structure. Most inorganic gases contain only 2 atoms, which leaves no question as to structure, except perhaps electron arrangement, and in ternary compounds, such as  $\text{CO}_2$ , valence considerations make us easily content with the decision that the carbon atom is between the oxygen atoms.

Dipole moment frequently furnishes valuable evidence concerning structure. For example,  $\text{CO}_2$  and  $\text{CS}_2$  both have zero moment, indicating symmetrical linear structures, OCO and SCS. Water, on the other hand, with a moment of  $1.85 \times 10^{-18}$  e.s.u., cannot be HOH but is  $\text{HO}$ , with an H

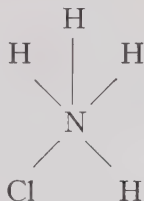
angle that has been estimated as  $105^\circ$ . Similar dissymmetry is concluded for  $\text{SO}_2$ ,  $\text{NH}_3$ , a pyramid rather than a triangle, ether,  $(\text{C}_2\text{H}_5)_2\text{O}$ , and many other molecules for which a symmetrical structure might be written.

One frequently finds structural formulas in inorganic substances, but they have usually been written by carrying over into inorganic chemistry the "bonds" of organic. Some chemists can look with equanimity upon such a structural formula as



for the "valences" look quite regular. Definite assertions as to structural formulas are sometimes made with no other basis than this. However, when we consider a salt such as  $\text{KAlCl}_4$ , we cannot write any structural formula which

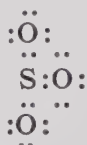
satisfies our older notions of bonds. In explaining  $\text{NH}_4\text{Cl}$  it used to be the practice to write



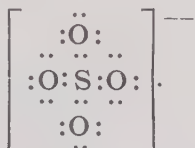
considering nitrogen pentavalent, as in  $\text{N}_2\text{O}_5$ , but when we come to  $\text{HF} \cdot \text{BF}_3$ , or  $\text{HBF}_4$ , we can hardly admit pentavalent boron. The failure of the bond in some cases casts doubt upon the correctness of formulas in which it appears to be consistent with valence.

Light was thrown upon the problem by the studies of Werner, who distinguished a second type of valence, the "**coördination number**," which expresses the number of atoms or radicals that tend to surround a central atom. This is seen in the complex ions, where  $\text{Cu}^{++}$ ,  $\text{Zn}^{++}$ , etc., although "bivalent," take on  $4\text{NH}_3$  in forming ammonia complexes, while  $\text{Ag}^+$  and  $\text{Cu}^+$ , "univalent," take on  $2\text{NH}_3$  or  $2\text{CN}^-$  in forming complexes. Werner pointed out the prevalence of a coördination number of 4, regardless of the charge of the central atom. Thus we might expect from the oxidation numbers of Cl, S and P that we should have the acids,  $\text{H}_7\text{ClO}_7$  or  $\text{Cl}(\text{OH})_7$ ,  $\text{H}_6\text{SO}_6$  and  $\text{H}_5\text{PO}_5$ . Instead we have  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ , a maximum of 4 atoms of oxygen in each case, regardless of changing valence.

Such facts as these are explained in terms of the electron structures of the atoms and the apparent stability of groups of 2 or 8 electrons. Thus the sulfur and oxygen atoms being  $:\ddot{\text{S}}:$  and  $:\ddot{\text{O}}:$ , respectively,  $\text{SO}_3$  is

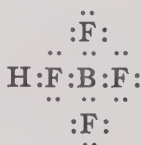


Now the sulfur atom has its oxidation number satisfied, but not its coördination number, that is, it is surrounded by only 6 electrons instead of 8. These can be supplied by sharing an electron pair of another oxide, such as  $\text{H}_2\text{O}$ , giving  $\text{SO}_4^{--}$ , whose structure should be

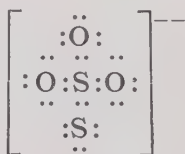


Since the 4 O and the S kernels have together an excess of + 30, and there are 32 valence electrons, there are 2 negative charges in excess. Obviously, the oxygen atoms are all alike and we cannot say that any particular electrons are the extra electrons. It would therefore be a matter of chance which oxygen atoms the hydrogen atoms would attach themselves to.

We can account for  $\text{HBF}_4$  by writing:



in which both the boron and the fluorine have their octets. The nature of  $\text{S}_2\text{O}_3^{--}$  is expressed by:



where the outer sulfur can be removed either with or without the pair joining it to the central sulfur, according as we have decomposition into  $\text{S}^{--}$  and  $\text{SO}_3$  or into S and  $\text{SO}_3^{--}$ . The 4 surrounding atoms are undoubtedly arranged tetrahedrally about the central atom.

In cases of coördination number of 6, Werner has prepared the number of isomers corresponding to an octahedral arrangement.

The above conclusions are in harmony with some remarkable experimental deductions as to the arrangements of atoms in crystals. When X-rays are passed through a crystal they are diffracted into definite patterns, cf. Fig. 3, just as a beam of light in passing through a finely ruled glass plate is broken up into a spectrum.

In the case of the crystal the atoms are responsible for the diffraction, and the patterns depend upon their arrangement in the crystal. This method was developed by Moseley, and later by W. H. Bragg and W. L. Bragg, who have given us thereby an extraordinary insight into the structure of matter. It shows that in a crystal of NaCl the charged

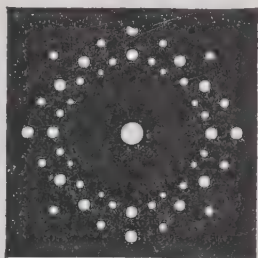


FIG. 3. Typical X-ray diffraction pattern.

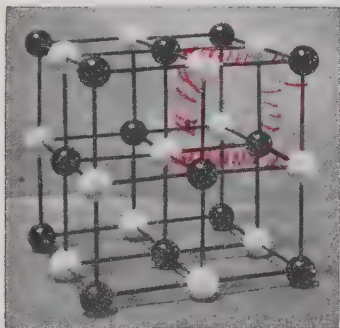
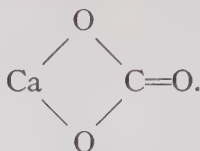


FIG. 4. Crystal structure of NaCl.

atoms are arranged in a cubic space lattice, as shown in Fig. 4, the  $\text{Na}^+$  and  $\text{Cl}^-$  alternating. Each sodium ion is surrounded at equal distances by 6 chloride ions, and *vice versa*. We cannot recognize any distinct molecules of NaCl. Evidently the forces of attraction between the ions are responsible for the cohesion of the crystal. Nearly all of the alkali halides follow

this pattern, also a number of oxides like  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{CdO}$ .

Calcium carbonate is similar in that calcium and carbonate ions alternate. All three oxygen atoms are equally spaced about the carbon atom, contrary to the demands of the structural formula which used to be given,



Furthermore, each calcium ion is equally close to its 6 surrounding  $\text{CO}_3$  ions. There is, therefore, no distinct molecule of  $\text{CaCO}_3$  in the crystal (cf. Fig. 5).

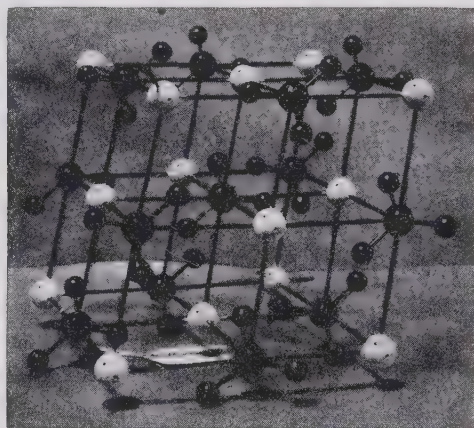


FIG. 5. Crystal structure of  $\text{CaCO}_3$ .

A number of metals crystallize with atoms at the corners of a cube and an additional atom in the center of the cube, the so-called "body centered" cube. These include sodium, chromium and the form of iron stable at low temperatures,  $\alpha$ -iron. The form of iron stable at high temperatures,  $\gamma$ -iron, has what is known as a "face centered" arrangement, with an atom of iron in the center of each cubic face as well as at each corner. It is interesting to note that the ordinary form of nickel has this same arrangement, which accounts for the fact that in nickel steel the  $\gamma$ -iron is stable at ordinary temperatures, so that to get it at low temperatures does not require the rapid cooling necessary to get ordinary steel in the hard form.



In diamond, Fig. 6, the atomic arrangement is less easily described, but is such that each carbon atom can attach itself by an electron pair to its 4 nearest neighbors. The 4 chemical bonds of carbon are thus all called into play, and since the carbon atoms are very small, and can get very

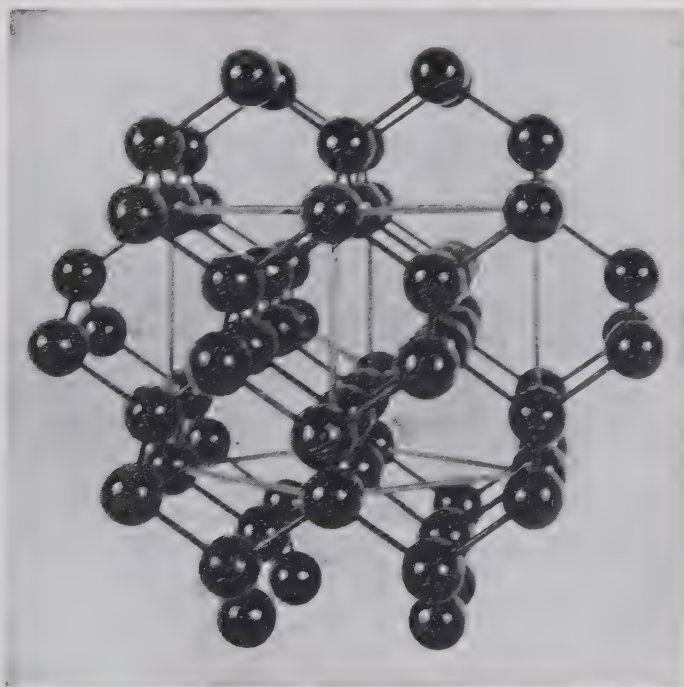


FIG. 6. Crystal structure of diamond.

close together, so that the forces between them are very large, diamond is the hardest of all known substances. It is possible to see in the diamond lattice the main structures of organic chemistry, viz., the tetrahedron, the zig-zag chain and the hexagon. The lattice of graphite, shown in Fig. 7, retains the chain and the hexagon, now flat, but has lost the tetrahedron. The flat planes are far apart and can slide over each other; hence graphite is a lubricant, in striking

contrast to diamond. It is also an electric conductor, due to the loosening of the electrons between the planes, and is much less dense than diamond.

In the crystal of an un-ionized substance, such as benzene, the molecules do not lose their identity, so that the

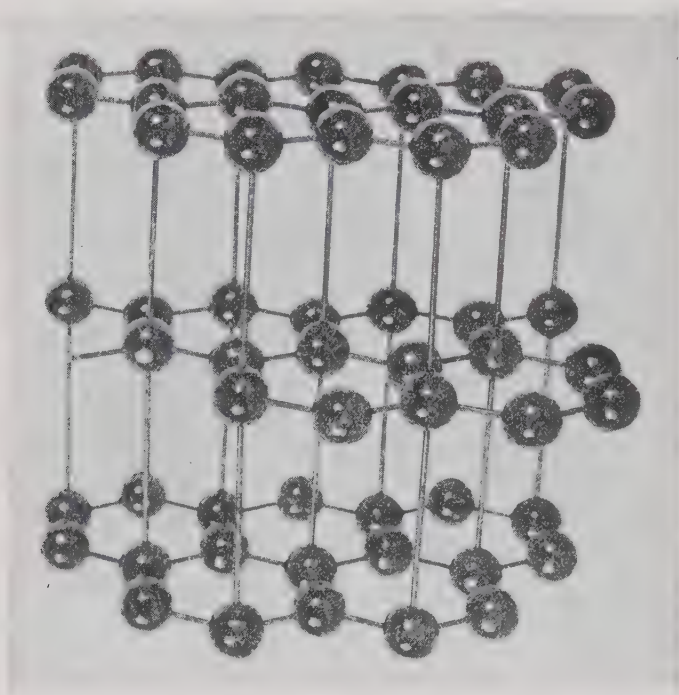


FIG. 7. Crystal structure of graphite.

same molecule which builds up a crystal comes off when the crystal dissolves or evaporates, unlike the NaCl crystal, where a sodium ion, in leaving the surface, might go off with any one of the surrounding chloride ions.

**25. The Proton Donor-acceptor System of Acids and Bases.** It was pointed out in Chapter V that there are at least three recognized methods of defining acids and bases. The ordinary system, appropriate particularly for aqueous

solutions, defines an acid as a substance yielding hydrogen ion,  $H^+$ ,  $H^+$  (aq.) or  $H_3O^+$ , and a base as a substance yielding hydroxide ion,  $OH^-$ ,  $OH^-$  (aq.) or  $O_2H_3^-$ . Neutralization is the union of these two ions to form the solvent, water. If a different solvent were used, say, liquid ammonia, an acid would be a substance giving the positive ion of the solvent, in this case  $H^+$ ,  $H^+$  (am.) or  $NH_4^+$ , and a base would give the negative ion, here,  $NH_2^-$ . For example,  $NH_4Cl$  would be an acid in liquid ammonia and  $KNH_2$  a base.

Chemists, particularly organic chemists, who work with a variety of solvents often find it advantageous to use a system which is less dependent on a particular solvent. The one preferred defines an acid in the same way as above, *i.e.*, as a substance capable of giving hydrogen ion, or proton, regardless of the kind or degree of solvation. A base is any substance which can unite with hydrogen, or "accept a proton." Hydroxide ion is thus only one of a large number of bases. Not only are all negative ions potential bases but certain neutral molecules, like  $NH_3$  and  $H_2O$ . The ions of the weakest acids are the strongest bases and *vice versa*. Table 2 gives a series of acids and their "conjugate bases" in order of decreasing acid for the former and increasing base strength for the latter. This order will, of course, be more or less influenced by the solvent.

TABLE 2

Strong		Acid				Weak		
$HClO_4$	$HCl$	$HOOCCH_3$	$Al^{+++}(aq.)$	$H_2CO_3$	$NH_4^+$	$HCO_3^-$	$H_2O$	$OH^-$
$ClO_4^-$	$Cl^-$	$OOCCCH_3^-$	$AlOH^{++}$	$HCO_3^-$	$NH_3$	$CO_3^{--}$	$OH^-$	$O^{--}$
Weak		Base				Strong		

The equilibrium between acid, A, and base, B, is always represented by the equation  $A = H^+ + B$ , where either A or B may have charges. The strength of either acid or base is expressed by the equilibrium constant for this reaction,

or, what amounts to the same thing, the concentration of  $H^+$  when the concentrations of A and B are equal. This avoids the necessity of any separate treatment for hydrolysis since an ion such as acetate which, in the ordinary sense, is hydrolyzed in water, is in the present sense itself a base possessing the power to reduce the concentration of  $H^+$  in the above equilibrium to a smaller value than it would have in water. Similarly, the hydrolysis of  $NH_4^+$  to produce the weak base  $NH_4OH$  and  $H^+$ , is more simply expressed in the present system in terms of the equilibrium:  $NH_4^+ = NH_3 + H^+$ , where the  $NH_4^+$  is an acid and the  $NH_3$  is a base. One of the most attractive features of this system is the approximate maintenance of the same order of strength of a series of acids and bases as we go from one solvent to another. This constancy is, however, extremely rough for it is obvious that solvents of different properties cannot affect the acid-base equilibrium in the same way for all substances.

**26. The Electron Donor-acceptor System**, likewise described in Chapter V, like the two preceding systems, involves chemical equilibria, as, for example



where the substance  $CaO$  is the base and  $CO_2$ , the acid. Here, as before, substances may be arranged roughly in order of acid and basic strength; but, as in the preceding case, this order cannot be rigid, for the bonding forces involved are often highly specific as seen, for example, in the preference for water rather than ammonia shown by most alkaline earth ions on the one hand, and the preference for ammonia shown by silver and copper ions on the other hand. This system is the most general of the three. The first limits both acids and bases to substances giving particular ions,  $H^+$  and  $OH^-$ ; the second limits acids to substances giving  $H^+$ , while bases are any substances which can unite with  $H^+$ ; the third removes the limitation to  $H^+$ , and

defines an acid as any substance which can perform the same function as  $H^+$  of uniting with an electron pair rapidly and reversibly.

### EXERCISES

- Write formulas of the following so as to show the constituent radicals.

(1) Propyl alcohol	(10) Pentadecane
(2) Methyl ethyl ether	(11) Dimethyl sulfate
(3) Dibutyl ketone	(12) Ethyl sulfide
(4) Amyl acetate	(13) Dipropyl oxalate
(5) An aldehyde containing two carbon atoms	(14) Methyl amine
(6) An acid containing six carbon atoms	(15) Propyl cyanide
(7) Hexyl chloride	(16) Dichloromethane
(8) Ethyl nitrate	(17) Trichloromethane
(9) Diphenyl ketone	(18) Glyceryl triacetate
	(19) Phenyl amine
	(20) Acetic anhydride
- Define: isomer, organic chemistry, aromatic compound, aliphatic compound, unsaturated compound.
- Give the principles used in determining the structure of organic compounds.
- What evidence is there that the benzene molecule has a ring structure?
- What difficulties are encountered in applying organic notions of structure to inorganic substances?
- What evidences are there for the structure of inorganic substances?
- What is a molecule of solid  $NaCl$ ? Of solid benzene?
- Suggest other substances which you would expect to be respectively polar and non-polar.
- Which should be more polar, (a)  $CH_3Cl$  or  $CH_3I$ ; (b)  $C_2H_6$  or  $C_2H_5Cl$ ?

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# Chapter XIX

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## *Dispersed Systems*

1. In Chapter I a distinction was made between heterogeneous and homogeneous material, between mechanical mixtures and solutions. If we have a bottle containing water in the lower portion and moist air in the upper, we would not hesitate to call the system heterogeneous. Even if the water were blown into the air from an atomizer, we would doubtless still consider the system heterogeneous. Suppose, however, we could break up the droplets into successively smaller and smaller ones, ending finally with molecules of water vapor in air. The system finally resulting we would have to consider as homogeneous. At what stage in the disintegration process, we may well ask, did the system cease to be heterogeneous and become homogeneous? We might imagine a similar gradation starting with sand and water, which would be heterogeneous, through successively finer and finer suspensions of silica powder in water until we would have a solution of silica molecules in water. There is, evidently, no sharp boundary between systems certainly heterogeneous, on the one hand, and solutions, on the other hand, and between these two extremes there are systems which should have some of the characteristics of both. These we will call **dispersed** systems, one phase being highly dispersed in another. The following scheme gives a survey of the types of dispersed systems, classified according to the nature of the phases. We distinguish, on the one hand, between the dispersed phase,



which is discontinuous, minute isolated particles, drops or bubbles, and the dispersing medium, on the other hand, which is continuous.

DISPERSED PHASE	INCLOSING PHASE	TYPE
Liquid	Gas	Fog
Gas	Liquid	Foam
Solid	Gas	Smoke
Gas	Solid	Solid foam ( <i>e.g.</i> , pumice)
Liquid	Liquid	Emulsion
Solid	Liquid	Suspension
Liquid	Solid	
Solid	Solid	Many alloys

In addition there are systems, such as sponge, charcoal and gelatin jelly where both phases are continuous, with a network structure.

The most important of these from a chemical standpoint are emulsions and suspensions, and our attention will be largely confined to them.

**2. Brownian Movement.** As the dispersed phase in suspensions and emulsions becomes more and more finely divided it is possible to get systems in which the two phases do not separate on standing under the influence of gravity. A relatively large body like a grain of sand, dropped into water, will fall through the water at a rate of speed dependent on its size, the difference in density between it and water, and the viscosity of the water. A very small sand particle will fall more slowly through the water, because as the size diminishes, the surface, upon which the resistance depends, does not decrease as fast as the weight. Fine suspensions, therefore, settle out more slowly than coarse ones. When a sufficiently minute particle is observed with a microscope it may be seen that it no longer falls in a straight line, but follows an irregular zigzag path. The reason for this is as follows: the molecules of water, according to the kinetic theory, are in rapid motion, with a mean kinetic

energy proportional to the absolute temperature. In disordered motion of this sort some molecules, at a given instant, will be moving more rapidly and some more slowly than the average. When the particle of sand is so large compared with the water molecules that it is being bombarded by a very large number of the latter, the effect of differences in their kinetic energy will be neutralized; but when the particle gets sufficiently minute, an especially

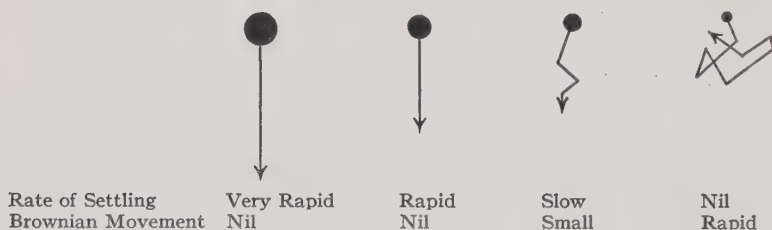


FIG. 1.

hard impact on one side of it may not be neutralized by the impacts of other molecules on the other side, hence the particle will be slightly displaced. Since these abnormally hard impacts are constantly occurring irregularly from different directions the result is the irregular zigzag movement of the particle above referred to. As smaller and smaller particles are taken, the chances for inequality in the momentum of the impacts upon them increase, and their resulting displacement also increases, for a molecule of water striking a small body will have more effect on it than upon a larger one. In fact it can be seen by the aid of the microscope that the particles of fine suspension are in much more violent motion than those of a coarse suspension. This progression is illustrated in Fig. 1. This movement is known from its discoverer as the **Brownian movement**, and gives us very direct evidence of the truth of the kinetic theory.

3. When sufficiently fine particles are taken, the Brownian movement overcomes the effect of gravity so that the

particles remain in permanent suspension. The system is then known as a **colloidal suspension**, or **colloidal solution**. There will be, in such a suspension, if time is allowed, an increasing concentration of particles from the upper to the lower portions of the vessel, analogous to the increasing concentration of the atmosphere from high altitudes to lower. In fact, a French physical chemist, Perrin, showed that the rate of increase in the concentration of the particles in suspensions obeys the same laws that govern the change in barometric pressure with altitude, a most striking proof of the truth of the kinetic theory and of the real existence of molecules.

4. The dividing line between suspensions which settle out on standing and colloidal suspensions, which remain permanently suspended, is purely one of convenience, for by applying centrifugal force it is possible to separate suspensions that would not do so under the influence of gravity alone. In general, colloidal suspensions cannot be separated by filtration through ordinary filters.

5. It is possible to distinguish in practice between true solutions and colloidal solutions or suspensions by aid of the great differences in their rates of diffusion. The Brownian movement of colloidal particles is so much less than the movement of the much smaller molecules of substances in true solution that the former diffuse from regions of greater to regions of smaller concentration with much less rapidity. The first distinction between the two types of solutions was made upon this basis by Graham, in 1862. He obtained the following figures for the time required for the equal diffusion of various substances:

HCl	1	MgSO <sub>4</sub>	7
NaCl	2.3	Albumen	49
Sugar	7	Caramel	98

To the class of substances which diffuse slowly he gave the name **colloids**, from the Greek name for glue, a member of this class.

6. The molecular weight can be calculated from the rate of diffusion and also from the lowering in vapor pressure or in freezing point, as explained in Chapter IV. These methods all agree in ascribing very high molecular weights to substances in colloidal solution, as is to be expected. The following figures illustrate the values found:

SUBSTANCE	MOLECULAR WEIGHT
Egg albumen. . . . .	20,000
Gelatin . . . . .	40,000
Pepsin . . . . .	12,000

7. **Optical Properties of Colloidal Suspensions.** When a colloidal suspension is viewed by transmitted light it usually appears homogeneous, like a true solution, its color depending on the size of the particles and on the nature of the material. By reflected light we usually notice a somewhat different color and an opaque, muddy appearance similar to that of ordinary suspensions. The microscope will detect particles as small as 0.000,25 millimeter in diameter. Smaller particles than this cannot be viewed directly as they are smaller than the wave length of light, so that the latter cannot be regularly reflected from them. It is possible, however, to detect the presence of particles as small as 0.000,006 millimeter by looking at them in a strong transverse beam of light against a dark background. (The diameters of the molecules of most ordinary substances are less than 0.000,001 millimeter.) Although no real image of the particle may be seen, there is a scattering of the light by it so that a bright speck of light can be seen in the microscope. The same effect is responsible for the visibility of a beam of light in a dark room through illumination of dust particles, invisible, perhaps, even in a microscope. A microscope arranged for use with a powerful transverse illumination against a dark background is called an **ultra-microscope**. By knowing the concentration of the material in a colloidal suspension, and counting the number of par-

ticles in a tiny beam of known dimensions it is possible to determine the average size of the particles.

**8. Adsorption.** Solid surfaces have the power of condensing gases upon them. The amount of gas so adsorbed depends upon the nature and area of the surface, the temperature and the nature of the gas. The lower the temperature the more slowly do the gaseous molecules move, and the more easily are they held by the attraction exerted by the solid surface. Hence the gases which are most easily condensed to the liquid state are also more highly adsorbed by solid surfaces. Of all gases helium, which boils at  $4.5^{\circ}$  A., is least adsorbed, followed by hydrogen, whose boiling point is  $20.5^{\circ}$  A., then by gases like nitrogen, oxygen, etc., then by ammonia, water vapor, etc. It is a fact familiar to chemical analysts that considerable amounts of water may be condensed upon the surfaces of pieces of apparatus like crucibles and glass beakers, so that it is necessary to have them in a dry atmosphere in order to get exact and reproducible weights. If the solid is porous, like charcoal, or finely powdered, its surface is vastly increased, allowing the same amount to adsorb very much more of the gas. The use of charcoal to adsorb odorous gases in this way is very familiar.

**9.** A similar adsorption of dissolved substances can take place from solutions upon solid surfaces immersed in them. "Boneblack," formed by the strong heating of ground bone, turning its animal matter into charcoal, is used in the refining of sugar to remove the yellow coloring matter present. The colored bodies are mainly substances with large molecules, which are readily adsorbed on the large surface of the boneblack, from which the solution of sugar can be filtered clear and colorless. Cottonseed oil is decolorized by fuller's earth in the same way. On account of the large surface exposed by even a small amount of solid in colloidal suspension (a cube having a diameter of 1 cm. and a surface of  $6 \text{ cm.}^2$ , if divided into cubes with a diameter of

0.0001 cm., would have a surface of 60,000 cm.<sup>2</sup>) the adsorption of dissolved substances upon the colloidal particles exerts an important effect upon their properties.

**10. Electrical Migration of Colloidal Particles.** An especially important effect upon the properties of fine suspensions is exerted by adsorbed ions. It is seldom that electrolytes are absent from aqueous suspensions, and even

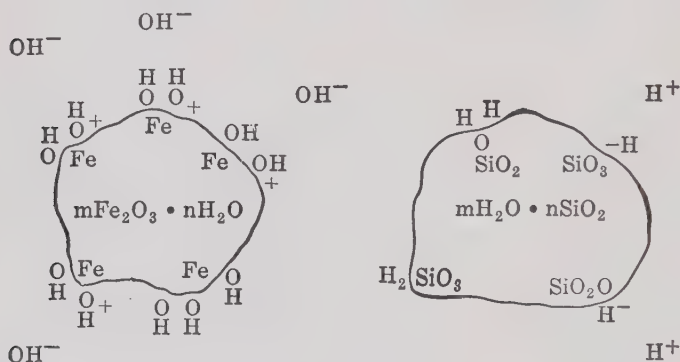


FIG. 2. Relation between chemical nature and sign of particle.

where such is the case, the ions of water may be differentially adsorbed. Certain kinds of suspensions are prone to adsorb positive ions in excess, whereby the particles acquire a positive charge, while others, in a similar way, become negative. As a result they are able to migrate with an electric current flowing through the solution, the direction depending upon the sign of the adsorbed ions. This phenomenon is known as cataphoresis. The speed with which they move is comparable to that of the slower ions, about 7 mm. per hour under a drop of potential through the solution of 1 volt per centimeter. It is thus possible to classify suspensions as positive or negative, just as the ions themselves were classified in Chapter VIII. Among the positive suspensions are those of the metallic hydroxides and sulfides; the negative suspensions include arsenous sulfide, silicic acid, graphite and the noble metals.



Figure 2 illustrates how the positive charge on ferric hydroxide results from its basic nature, while the negative charge on silicic acid corresponds to its acid character. There is no essential difference between adsorption of  $\text{OH}^-$  and adsorption of water followed by ionization of  $\text{H}^+$ .

**11. Relation between Charge and Stability. Coagulation.** Even though a suspended particle may be so small that its Brownian movement prevents its settling out under the influence of gravity, a suspension of such particles may not be stable, because of the tendency of the particles to adhere to one another on impact, forming successively larger aggregates until settling out can occur. This process may be seen when silver chloride is formed by mixing its ions. At first a very fine suspension is formed, which, if not too concentrated, appears quite stable, and may run through an ordinary filter. On standing, however, and more rapidly if the solution is heated and stirred, these extremely fine particles adhere to each other, forming eventually the familiar curdy precipitate of silver chloride. Now the effect of electrolytes upon the stability of such a suspension is very great. The presence of a charge upon the particles tends to make them repel each other and to prevent coagulation, so that a small amount of the proper electrolyte increases the stability. Suppose that we are dealing with a negative colloid, like  $\text{As}_2\text{S}_3$ . If some electrolyte is added whose positive ion tends to be highly adsorbed, it may partly displace the ion giving the negative charge, leaving the particle neutral and free to coagulate with others like it.

**12.** Hydrogen and hydroxide ions are usually highly adsorbed, so that the addition of a small amount of acid to a suspension of arsenous sulfide suffices to coagulate it, while the addition of a small amount of alkali to a positive suspension like that of ferric hydroxide coagulates it completely. In general, then, negative suspensions are coagulated by acids and positive suspensions by alkalis. There appear to be no

striking differences in the extent to which most other ions are adsorbed, but the effect of the valence of the adsorbed ion upon its ability to coagulate a suspension is very great. Let us suppose that  $\text{Na}^+$ ,  $\text{Ca}^{++}$  and  $\text{Al}^{+++}$  are adsorbed by suspended  $\text{As}_2\text{S}_3$  to the same degree. It is evidently not the amount of substance adsorbed but the amount of positive charge that it carries with it that determines its ability to neutralize the charge on a negative suspension. To have the same amount of electricity adsorbed, we will need but half as much of the doubly charged  $\text{Ca}^{++}$ , and but one third as much of the triply charged  $\text{Al}^{+++}$ , as we will of the singly charged  $\text{Na}^+$ . Hence it will take very much less  $\text{Ca}^{++}$  and still less  $\text{Al}^{+++}$  to have the same effect as a given amount of  $\text{Na}^+$ . Moreover, it is the amount adsorbed, and not the amount in solution, that determines the coagulating effect, and since the concentration of a substance in solution increases more rapidly than the amount adsorbed, the concentration of  $\text{Na}^+$  in the solution must be considerably more than three times that of the  $\text{Al}^{+++}$  in order that the amount of the former adsorbed be three times the latter.

13. Aluminum sulfate is extensively used in connection with filtration plants to increase the efficiency of the filtration on account of the great coagulating power of aluminum ion upon the negative suspension of mud in water. The aluminum hydroxide formed by the hydrolysis of the aluminum sulfate is itself a positive colloid, and also aids considerably in the coagulation, since a positive colloid acts like a positive ion in neutralizing the charge on a negative suspension.

14. The ions in sea water have a similar coagulating effect upon muddy river water discharged into it, a factor which aids in the formation of bars at river mouths.

15. Most dyes are very fine suspensions, which are themselves adsorbed or absorbed in animal or vegetable fibers. When the fiber is unable to hold the dye permanently, the

color may frequently be made "fast" by using a coagulant, called a "mordant." The mordant is the salt of an ion with a multiple charge like  $\text{Al}^{+++}$  or  $\text{Sn}^{++++}$ , which can diffuse into the fiber and hydrolyze, giving a positive hydroxide, which can hold the dye firmly. A "lake" is a pigment made of such a coagulum of a hydroxide, like  $\text{Al}(\text{OH})_3$ , with a suitable dye. The "purple of Cassius" is a similar coagulum of gold and stannic hydroxide, formed simultaneously in the reaction of stannous ion with chlor aurate ion, as follows:



**16.** In washing precipitates it is often found that the precipitate tends to become suspended and run through the filter. It is possible to prevent this re-suspension by washing with water containing a little acid, or ammonium salt, or ammonia, etc., as the case requires.

**17.** The effect of the charge of negative ions in coagulating positive suspensions follows the principles laid down for the corresponding effect upon negative colloids. Ferric hydroxide suspension, for example, is more easily coagulated by sodium sulfate than by sodium chloride.

**18. Emulsions.** We have thus far been considering dispersed systems in which a solid is suspended in a liquid. We will now consider those systems, called emulsions, in which the suspended phase is a liquid. Much of what has been said in regard to solid suspensions applies here. When the suspended droplets are small enough, as in cream, they are subject to Brownian movement, though in this case not sufficient to prevent their slow rise to the top by reason of gravity. The optical properties of emulsions are similar to those of suspensions. It is possible, however, to have stable emulsions with the suspended material less highly dispersed and in larger amounts than is the case ordinarily with solid suspensions, as illustrated by cream and mayonnaise dressing. In order to do this, however, an emulsifying agent

must be used, for two pure liquids will not form a stable emulsion. The reason for this is as follows:

When two suspended droplets come together they will tend to coalesce into one, for the surface tension operates to make the surface as small as possible, and one spherical drop will have less surface than two of the same total volume. In order to prevent their coalescing it is desirable to have the liquid in which they are suspended viscous, but especially is it necessary that the film of liquid which separates them when they are close together should be difficult to rupture, like the soap film which prevents two adjacent air bubbles from coalescing. Now a stable liquid film can be produced by some substance which greatly lowers the surface tension of the liquid. An exact proof of this could be given, but the following simpler explanation may suffice. The diminution in the surface tension is an evidence that the substance added diminishes the attractive forces of the molecules within the liquid; consequently there will be a tendency for molecules of the solvent to restore the condition of the pure solvent, where the molecules are probably closer together, by squeezing out, as it were, the molecules of the solute, which will therefore tend to be concentrated at the surface, still further lowering the surface tension. In fact we find that the surface tension of soap solutions is much less than that of water, and also that the tension at a surface that has stood for a short time is less than it is at a fresh surface, as illustrated by the following figures:

SURFACE TENSION		
	FRESH SURFACE	OLD SURFACE
Water . . . . .	79	79
1.25 per cent soap solution . . . . .	62	26

19. Suppose, now, that we consider a film of such a solution, representing in Fig. 3, at *a*, the greater concentration of the soap at the surface by the shading. If a strain is put

upon the film so that it starts to rupture at a certain place, represented at *b*, the effect is to bring from the interior to the surface at this point solution in which the soap is at first less concentrated, and whose surface tension is, therefore, *greater* than that of the old surface. Consequently, whenever rupture threatens, the film becomes automatically stronger, and hence is stable. Sufficient soap dissolved in



FIG. 3. Automatic strengthening of a stretched soap film.

water will therefore give either a stable foam, if shaken with air, or a stable emulsion if shaken with oil. Other substances, like saponin, gelatin, albumen, the casein of milk, etc., may have the same effect in greater or less degree. The substances in the egg act in this way in making mayonnaise. Milk, when concentrated in the form of evaporated milk, can serve also for making mayonnaise.

It is possible to have either phase the inclosed phase, the oil being the inclosing phase in mayonnaise that has "separated," and in the water-petroleum emulsions that often give trouble in oil refining.

20. It follows from the foregoing theory that the type of emulsion favored will be the one in which the emulsifying agent is soluble in the outer phase, the one in which stable films are desired. Thus, sodium soaps favor oil-in-water emulsions, while aluminum soaps favor water-in-oil.

There is a tendency, also, for the phase present in smallest amount to be the inclosed phase, and one of the secrets of success in making mayonnaise is accordingly to wet the sides of the vessel with egg, and to add the oil slowly at first.

Further assistance is given by using a vessel whose material is better wet by the outer phase, *e.g.*, glass or china rather than metal.



**21. Differential Wetting.** The different degrees of wetting between liquids and solids is often quite evident. Everyone is familiar with the fact that tiny globules of mercury roll about on a wood surface; that water globules are only partly flattened out on a paraffin surface while they spread completely on clean glass. The difference between a clean and a greasy windshield is well known to all auto-

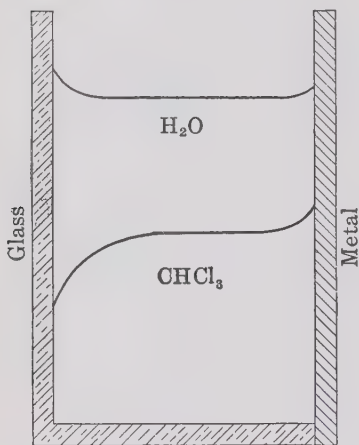


FIG. 4. Differential wetting.

mobile drivers. The simple experiment illustrated in Fig. 4 shows the tendency of water to displace chloroform on a glass surface while chloroform displaces water on a bright metal surface. Accordingly, if metallic powder were dropped onto the interface between these liquids, it would descend into the chloroform while glass powder would be floated on the interface, supported by the surface tension.

If one liquid does not completely displace the other, but the interface forms some finite angle of contact, the particles may remain in the interfacial surface, but protruding more into one liquid than into the other. If the less-wetting liquid is in drops, the adhering particles will then be mostly on the outside of the drop, and can serve as a sort of armor to hold drops apart and prevent coalescence. Solid powders may thus serve as emulsifying agents, the type of emulsion being determined by relative wetting as just explained. Figure 5 illustrates an emulsion of toluene in water by the aid of powdered pyrite,  $\text{FeS}_2$ , which is wet somewhat better by water than by toluene. The particles of pyrite can be seen coating the droplets, sticking to them but mainly in the water. Figure 6 shows the water as the inside phase in kero-



sene, brought about by using powdered charcoal, wet better by kerosene than by water.

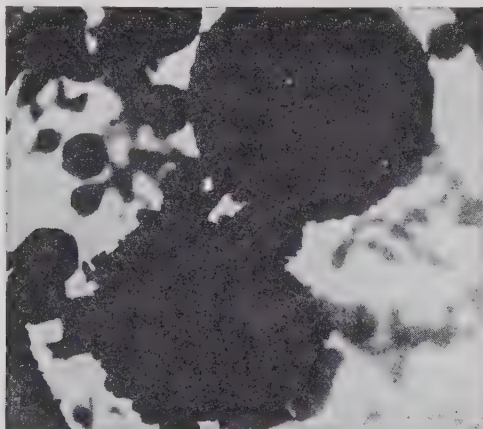


FIG. 5. Toluene emulsified in water by powdered pyrite.

Particles of metallic sulfide ores can be effectively purified from accompanying earthy material by grinding the

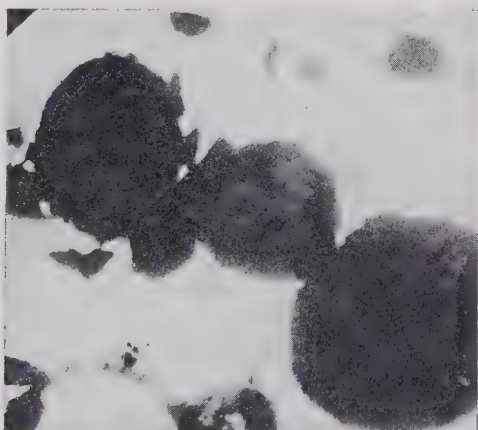


FIG. 6. Water emulsified in kerosene by powdered charcoal.

crude ore with a suitable oil and water, suspending the mass in water to which a foaming agent has been added and blowing air bubbles up through the suspension. The oil-coated

metallic particles trying to escape from the water, attach themselves to the bubbles and are carried out over the rim of the tank where the froth is broken down and the pure ore recovered; the water-wet earthy impurities remain in the tank. This process is known as **ore-flotation** and has greatly increased the efficiency of ore-recovery.

**22. Lyophilic Colloids.** There are a number of colloids, most of which are obtained directly or indirectly from plant or animal organisms, which readily remain in combination with water or some other appropriate solvent. These include albumens, soaps, gums, tannins, starch, gelatin, glue, caramel, rubber and nitro-cotton (nitro-cotton is extensively used in making collodion, celluloid, smokeless powders, varnishes and artificial leather). These substances instead of being difficult to bring into solution and easy to coagulate, like most colloidal suspensions, give solutions or jellies very rapidly. Where water is the dispersing liquid, as with albumen or gelatin, the colloid may be called **hydrophilic**, signifying that it is a "lover of water," and in distinction to the **hydrophobic** colloids such as arsenous sulfide. Where some other dispersing medium than water is used the more general terms **lyophilic** and **lyophobic** may be used, signifying respectively "lover" and "hater" of the solvent. Thus nitro-cotton is lyophilic to a mixture of ether and alcohol but lyophobic towards water.

These colloids have also been called "reversible colloids," because, like gelatin, they can usually be easily redissolved after drying out. Again they have been called "emulsion colloids" since they behave in many respects like emulsions. It seems rather certain, however, that in many cases the dispersed phase is not in the form of droplets, but consists rather of threads which stretch through the solution forming a network. Such solutions, even when very dilute, often have a very high viscosity, and when more concentrated yield a jelly. Ions may migrate through a gelatin jelly almost as rapidly as through water.

**23.** Some of these substances, such as gelatin and albumens, are made up of amphoteric molecules containing both carboxyl and amino groups. These can unite with each other indefinitely to give the large colloidal aggregates or the solid jelly structure. The addition of either acid or alkali tends to break up the aggregates, decreasing viscosity and making the solution more difficult to gelatinize. If the jelly does not melt upon treatment with acid or alkali it at least swells by taking up more water.

Since most of the material of which living organisms are made is colloidal in nature, it will be perceived that the subject of colloids becomes one of great importance to the biologist.

**24. Protective Colloids.** If an oil emulsion were mixed with a metallic suspension, the oil drops would tend to inclose the metal particles, and the resulting system would behave essentially like a pure emulsion. Similarly, when an emulsion colloid, or hydrophilic colloid, is mixed with a hydrophobic colloid, the mixture behaves like a colloid of the former class. Since the hydrophilic colloids are relatively stable, a hydrophobic colloid may be made stable in this way. For example, if gelatin is present in a solution in which silver chloride is formed from its ions, each particle of the silver chloride is coated with gelatin so as to prevent the coagulation that would otherwise ensue. The retention of this highly dispersed state in the solidified gelatin makes possible the photographic dry plate. Again, when gelatin is added to a suspension of arsenous sulfide it requires much more concentrated acid to coagulate it.

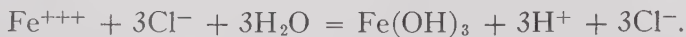
**25. Preparation of Colloidal Solutions.** In addition to the colloids obtained from biological sources, such as gelatin, albumens, starches, etc., it is possible to prepare highly dispersed systems of other materials by various methods, which may be classified as dispersion or condensation methods, according, respectively, as we start with undispersed material or with molecularly dispersed material, molecules and ions.

(a) **Dispersion Methods.** Colloidal solutions of the nobler metals may be prepared by passing an arc between electrodes of that metal under water. The metal is vaporized in the arc and the vapor is condensed to solid particles in a highly dispersed state.

Previously coagulated material may often be redispersed by washing out the coagulant, as occurs in washing certain precipitates. Basic ferric acetate, precipitated by boiling a solution containing ferric acetate, may be redispersed by washing with water containing a trace of acid.

Some substances can be dispersed by the aid of a "peptizer," usually a protective colloid, taking its name from the action of pepsin in dispersing albuminous material in the process of digestion. Thus graphite can be peptized, or suspended, by grinding it with tannin. The resulting solution is known commercially as "aquadag," and can be used as a lubricant. The cleansing action of soap, which is in the colloidal state when dissolved in water (not when in alcohol), is of this nature.

(b) **Condensation Methods.** By starting with ordinary solution it is possible to get suspensions by suitable means. Thus a solution of a ferric chloride always contains free  $H^+$ ,  $Cl^-$  and  $Fe(OH)_3$  (or basic chloride), the last of which is partly agglomerated, so that it will not pass through a very fine membrane like parchment. Accordingly, if such a solution is separated by parchment from pure water, the  $H^+$  and  $Cl^-$  can diffuse out. The  $Fe(OH)_3$  accumulates as the hydrolysis proceeds, as represented by the equation,



By continually renewing the water into which the hydrochloric acid diffuses, the hydrolysis may be made complete, leaving a colloidal solution of ferric hydroxide. Such a process of separation by differential diffusion is called **dialysis**. Other hydroxides can be obtained in colloidal

solution by the same method. That a colloidal solution is obtained by dialysis but not by the addition of alkali, is due to the coagulating effect of the hydroxide ion which would be present under the latter circumstances.

Whenever a relatively insoluble substance can be produced in the absence of any considerable amount of electrolytes, it is possible to prepare it as a colloid. Thus the action of  $\text{H}_2\text{S}$  on a solution of  $\text{As}_2\text{O}_3$  will give a suspension of  $\text{As}_2\text{S}_3$ , since the substances involved are all practically un-ionized. A suspension of  $\text{HgS}$  can be obtained by the action of  $\text{H}_2\text{S}$  on  $\text{Hg}(\text{CN})_2$  for the same reason. Colloidal gold can be prepared by the reduction of a very dilute solution of  $\text{HAuCl}_4$  by some non-ionized reducing agent, such as formaldehyde,  $\text{CH}_2\text{O}$ , or a solution of phosphorus in ether. The addition of some protective colloid, like gelatin, allows the solution of the metal to be prepared in much more stable form, and also more concentrated. The "argyrol," used in treating cold in the head, is a concentrated protected solution of colloidal silver.

### EXERCISES

1. Discuss the conditions necessary for the existence of stable foams and emulsions.
2. Summarize the characteristics of hydrophilic and hydrophobic colloids, respectively.
3. Assuming that you have discovered that a certain colloid migrates with the positive current, decide whether it would be coagulated more easily by  $\text{HCl}$  or  $\text{NaOH}$ .
4. When a substance is dispersed in a liquid the behavior of the system will depend mainly upon the following factors: (a) the size of the dispersed particles, (b) the magnitude of the surface tension between the phases, (c) whether the dispersed phase is solid or liquid, (d) whether the dispersed particles absorb positive or negative ions more readily. Decide what effect, if any, each of the above factors would have upon each of the following phenomena: (1) the Brownian movement, (2) the electric migration, (3) the rate of diffusion, (4) coagulation, (5) separation on standing, (6) absorbing power, (7) protective action on other dispersed substances.

-5. What conditions should be observed in the formation of colloidal solutions?

6. Outline experiments to enable you to determine the most effective means for coagulating a colloidal suspension of an unfamiliar substance.

7. Make a classification of dispersed systems that will, in your opinion, best express their various behaviors.



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# Chapter XX

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## *Solubility*

1. The property of solubility is one of the most interesting and important of physico-chemical phenomena. Some phase of it is encountered frequently, not only in everyday life, but in industry and scientific investigations. To remove from clothing a grease spot, a grass stain or a smear made by sitting on a chocolate cream requires a different solvent in each case. Most chemical reactions occur in solution and appropriate solvents must be selected. Separations, both analytical and industrial, are effected chiefly by the aid of differences in solubility. Molecular weights often cannot be determined by vapor density since the temperature necessary for vaporization may be so high as to be inconvenient or cause decomposition; we may then determine it in solution and must know, of course, how to choose an appropriate solvent. Again, materials for vessels should be made of substances as insoluble as possible in the liquids likely to be put therein. In order to understand such phenomena, it does not suffice to commit to memory a few simple rules, for the factors involved are numerous and often complicated. It is likely to be profitable, nevertheless, to consider some of the more important factors and to gain some notion of the general methods of attacking these problems.

2. As a first step, we may recall the classification of molecular types previously given (Chapter V, paragraph 10) into non-polar, polar and ionic molecules. Each molecular

type crystallizes in a corresponding solid lattice, also set forth in an earlier chapter (Chapter V, paragraph 13). We may recall, furthermore, the general nature of the process of solution for each of these lattice types (Chapter VIII, paragraph 2) and proceed

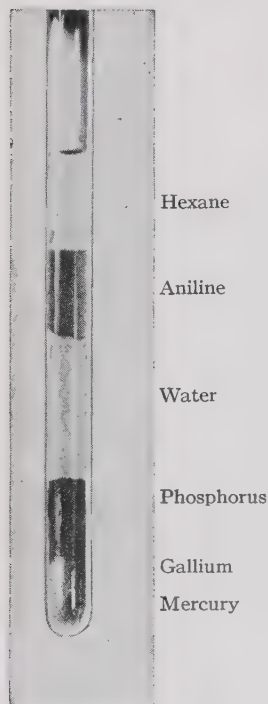


FIG. 1. Six stable liquid layers.

now to a more detailed discussion of each. We shall find that not only is solubility determined by the type of molecule and intermolecular force, but also by its strength. By way of illustration of the variety possible when we are able to vary both the strength and the type of intermolecular field, we may consider the system illustrated in Fig. 1, showing six substances sufficiently insoluble in each other to exist in six distinct liquid layers. This is a truly stable system and does not depend for the existence of layers upon mere slowness of diffusion, but would be reformed even though the system were shaken.

**3. Non-polar Molecules.** Molecules which are uncharged, and non-polar are able to attract each other only because of disturbances produced by mutual interaction of their

rapidly moving electrons. This disturbance has no exact counterpart in ordinary mechanical systems, but is remotely analogous to the interaction that would exist between two vibrating tuning forks. The magnitude of the force between a pair of such molecules depends on the total number of electrons in the molecule and the looseness with which they are held; also upon the closeness of approach possible before repulsion between them sets in. The force

falls off approximately with the seventh power of the distance between the molecular centers, and therefore practically disappears when a pair of molecules are only two or three molecular diameters apart. When two molecules come sufficiently close to each other, "repulsion" sets in, with something like a tenth or twelfth power of the distance. Molecules are, of course, not absolutely rigid, hard spheres. Figure 2 illustrates how the attraction between a pair of molecules grows rapidly at first as the distance between them diminishes and then turns very abruptly into repulsive force. A comparison of curves *A* and *B* shows how the substance represented by *A* may have a higher intermolecular attractive force at the same distance than the

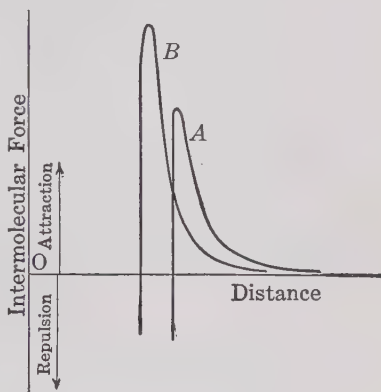


FIG. 2.

substance represented by curve *B*; nevertheless the force between the molecules for *B* may actually be greater than for *A*, on account of their closer approach to each other. It is not easy to measure the force existing between single pairs of molecules, and it is actually more important, of course, to consider the total resultant forces existing within a mass of liquid. This bears a relation, too complex to be explained here, to the forces between pairs of molecules which shows that it is possible to measure the total attractive energy existing within a mass of liquid by the energy of vaporization per cc. of liquid or the energy of vaporization per mole divided by the molal volume of the liquid at the temperature at which the vaporization takes place. This is often called the "**internal pressure**" of the liquid. Table 1 gives the values of this quantity for a number of more or less familiar substances. A few of them are sub-

stances which ordinarily exist as solids at 25°, and the values given are for the supercooled liquid, which is unstable with respect to the solid at this temperature. The substances have been arranged in order of increase from the top to the bottom of the table.

4. The significance of this order of arrangement is as follows: Liquids which are close together in internal pressure are able to mix with each other with very little difference between the attractive forces of the like and the unlike molecules. A given molecule, therefore, has about the same tendency to escape into the vapor phase from a solution as it would have from its own pure liquid; hence the number of molecules in the vapor phase is proportional to the mole fraction of them in the liquid. This law, known as **Raoult's Law**, may be written

$$p = p^{\circ}N$$

where  $p$  equals the partial vapor pressure of the substance from the solution,  $p^{\circ}$  is its vapor pressure in the pure state and  $N$  is the mole fraction of that species in the solution. In cases where this law holds, it is possible to calculate solubility from the above equation, not only of vapors, but also for gases and solids.

5. **The solubility of a gas** is usually expressed in terms of the amount which dissolves when the gas is at 1 atmosphere partial pressure over the solution. In such a case

$$p = 1 \quad \text{and} \quad N = 1/p^{\circ}.$$

$p^{\circ}$  is in this case the vapor pressure of the pure gas over its own liquid and is higher the lower the boiling point or critical pressure of the gas. If the temperature in question lies above the critical pressure of the gas, of course  $p^{\circ}$  has no obvious physical meaning. A fictitious value for it, however, can be derived by extrapolating the vapor pressure above the critical temperature. For making such an extrapolation, a plot of the logarithm of the vapor pressure

TABLE 1  
INTERNAL PRESSURE AND SOLUBILITY

Liquid	VOLUME PER MOLE, CC.	ENERGY OF VAPORIZ., CALS. PER CC.	SOLUBILITY, MOLES PER 100 MOLES OF SOLUTION					
			H <sub>2</sub> (20°)	N <sub>2</sub> (20°)	Cl <sub>2</sub> (0°)	I <sub>2</sub> (25°)	S <sub>8</sub> (25°)	P <sub>4</sub> (25°)
n-Heptane . . .	147.6	54.0	—	—	0.270	0.68	0.14	—
Ethyl ether . . .	104.5	55.5	0.061	0.124	—	—	.30	0.82
Silicon tetrachloride .	115.3	57.3	—	—	.288	.50	—	—
Carbon tetrachloride .	97.1	72.9	.032	.063	.298	1.15	.50	—
Chloroform . . .	80.7	79.7	—	.043	—	2.28	.57	—
Benzene . . .	89.3	83.6	.025	.043	—	4.82	.64	2.28
Chlorine . . .	50.9	87.7	—	—	—	—	—	—
Carbon disulfide . .	60.7	99.6	.008	.013	—	5.76	13.8	93.
Bromine . . .	51.2	135.	—	—	—	—	—	—
Sulfur . . .	136.	136.	—	—	—	(21)	—	—
Iodine . . .	59.2	190.	—	—	—	—	(28)	—
Phosphorus (active) .	70.4	194.	—	—	—	—	—	—

of the gas against the reciprocal of the absolute temperature can be used; this gives a straight line from which the extrapolation can easily be made to some higher temperature. Table 1 contains, for illustration, the solubilities of three gases, hydrogen, nitrogen and chlorine. Their boiling points increase in that order, and their solubilities, as will be seen from the table, increase in the same order. To put it in another way, chlorine is the gas most easily condensed to a pure liquid and hydrogen is the one most difficult to condense. Correspondingly, chlorine is most readily condensed into a solution and hydrogen least readily.

6. We see from the values in the table for the solubilities of hydrogen and nitrogen, that these values decrease as we go from liquids of lower to liquids of higher internal pressure. The explanation of this trend lies in the fact that the molecules of hydrogen and of nitrogen have very low fields of force, and hence they are able to penetrate most readily into liquids in which the forces of attraction between the molecules are low. As we descend the table to liquids of higher internal pressure, such as carbon disulfide, it is difficult for hydrogen and nitrogen molecules to get in between the molecules of solvent, hence their solubility is low. Chlorine, on the other hand, although a gas at ordinary temperatures, has small molecules and we see from the value of the energy of vaporization per cc. that the attractive forces between chlorine molecules are rather high; consequently, this substance dissolves most readily in the liquid nearest to it in the table, and its solubility falls off in both directions.

7. **Solids.** Iodine, sulfur and phosphorus have very high attractive fields; hence they mix most readily with liquids near them toward the bottom of the table, and their solubilities decrease as we ascend the table,—the opposite order to that found for hydrogen and nitrogen. Accordingly, we could fill in missing values in this, or even in a more extended table, with a considerable degree of confidence. For



example, the solubility of sulfur in silicon tetrachloride should doubtless be a little more than 0.3 mole per cent. The solubility of phosphorus in carbon tetrachloride may be expected to lie between 1 and 2 mole per cent.



8. The solubility of a solid, in the absence of chemical reactions, will normally be a maximum in a solvent which is close to it in internal pressure. This is true, for example, with sulfur and iodine, which do not react chemically. In such a case, the solubility in terms of mole fraction,  $N$ , can be calculated at a given absolute temperature,  $T$ , from the heat of fusion of the solid solute,  $\Delta H$ , at its melting point,  $T_m$ , by the following equation:

$$\log N = \frac{-\Delta H(T_m - T)}{4.58T_m T}.$$

The equation corresponds to the fact, which should be more or less obvious, that the higher the melting point of the substance and hence the harder it is to melt it to its own pure liquid, the harder it is, likewise, to get it to enter into a liquid state in some other solvent; hence the solubility of a substance normally decreases with temperature, and a substance with a lower melting point is more soluble. A large value for the heat of fusion of the solute likewise tends to diminish solubility. If we are considering a solvent and a solute which have rather different internal pressures, then the solubility will be normally less than that calculated by the above equation. This is illustrated by the decrease in the values for the solubility of iodine, sulfur, and phosphorus in the liquids higher up in the table.

9. The effect of melting point on solubility is beautifully illustrated by the comparison, shown in Table 2, between phenanthrene and anthracene, two substances which have the same composition,  $C_{14}H_{10}$ , differing only in the arrangement of the carbon atoms as shown in the table. The hexagons of carbon atoms are in a straight line in the latter but not in the former. The result is that the anthracene mole-

TABLE 2

		MOLAL VOL. CC.	MELT. PT.	SOLUBILITY MOLE PER CENT AT 25° IN BENZENE	BOIL. PT.
	Phenanthrene	174	99.6	18.6	340
	Anthracene	142	218.	0.63	342

cules pack much more closely in the solid crystal, as shown by the volume. They therefore attract each other more strongly, so that this substance both melts at a higher temperature and dissolves in all solvents to a far smaller extent.

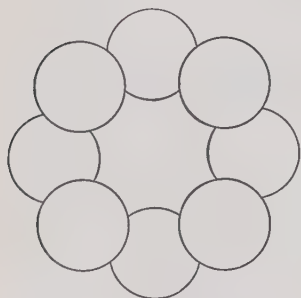


FIG. 3. Sulfur molecule.

To appreciate this, you have only to recall how much better your trout fit your frying pan before they are cooked than they do later, when they curl up. It is interesting to note that the two substances here considered, although they have very different melting points, have practically the same boiling point. This we may attribute to the fact that at high temperatures

there is sufficient thermal motion so that the liquid in either case consists of molecules jumbled up in all positions.

10. An interesting contrast in solubility is presented by two forms of sulfur. The molecules of ordinary sulfur consist of octagonal rings of atoms, represented in Fig. 3. These molecules retain their identity when dissolved. When these crystals are melted at 115°, the same octagonal molecules persist for a while. As the temperature is raised, however, the more violent agitation gradually knocks the rings apart, with the formation of chains of varying lengths. These chains become entangled with each other, so that the liquid becomes very viscous, quite contrary to the usual

behavior of liquids on heating. If we heat the sulfur still further, it gradually becomes more fluid as the chains become shorter, but if suddenly cooled by pouring into water, the rings do not have time to reform and the chains are "frozen." The chains are zigzag and can be extended by pulling, and the mass consequently behaves like rubber. The sulfur in this form is not soluble, since the chains are

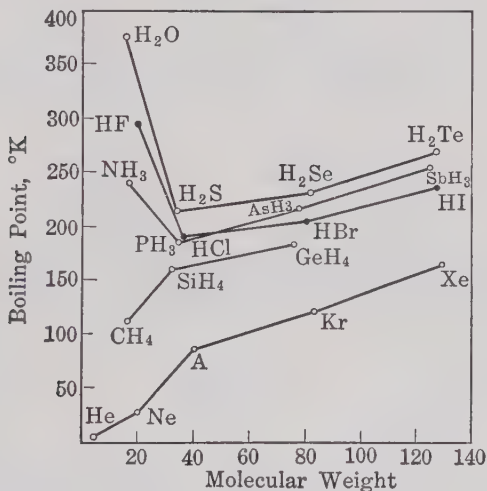


FIG. 4. Effect of hydrogen bonds on boiling point.

all tangled up like a mass of tangled string and small soluble units are not detachable.

**11. Polar Molecules.** Polar molecules cannot be expected to fit rigidly into the relation between internal pressure and solubility shown in Table 1, and discussed in preceding paragraphs. In many cases, however, departures from the preceding regularities are absent or small. This is particularly the case for substances whose electric dipoles are fairly well buried within the molecule, as is the case with ether and with chloroform, both of which possess considerable dipole moment but fit, nevertheless, very well into the series of internal pressures and solubilities. In other cases

the polarity may have considerable significance. Table 3 gives the comparison between the dipole moments of propyl chloride, propyl bromide and propyl iodide and

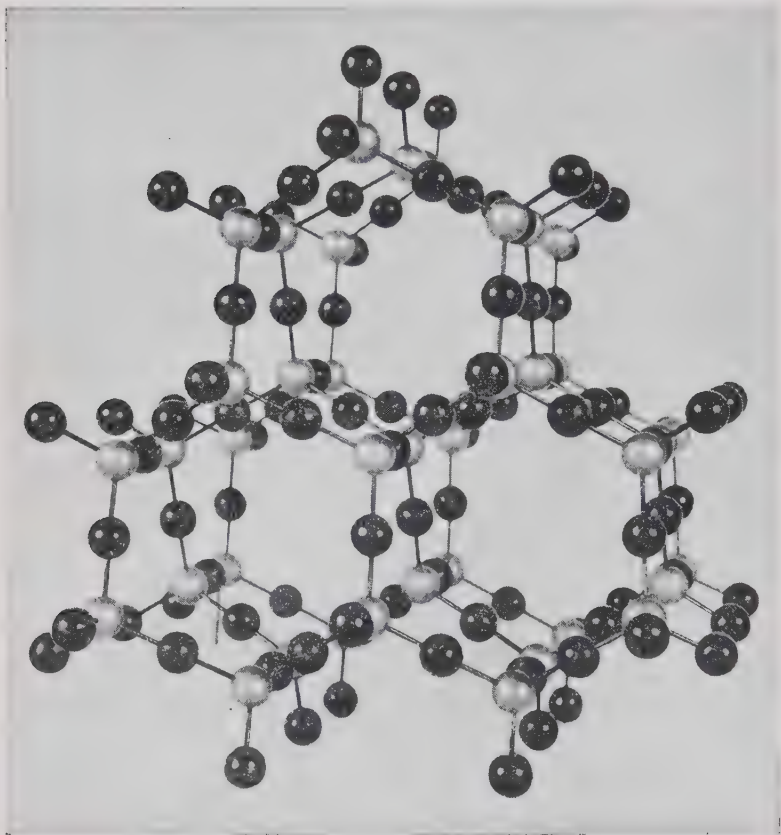


FIG. 5. Structure of ice. The light spheres represent oxygen atoms, the dark ones, hydrogen. It is evident that melting, which partly breaks up this structure, permits a closer packing and therefore higher density.

their solubility in water. Water, as explained elsewhere in this book, is a highly polar substance, and it is not surprising, therefore, that the solubility of the propyl chloride in water is the greatest, due to its possessing the highest dipole moment.

TABLE 3

	DIPOLE MOMENT $\times 10^{18}$ E.S.U.	SOLUBILITY IN WATER. PER CENT AT 20°
Propyl chloride, $C_3H_7Cl$ . . .	2.0	0.27
Propyl bromide, $C_3H_7Br$ . . .	1.8	0.24
Propyl iodide, $C_3H_7I$ . . . .	1.6	0.11
Propyl alcohol, $C_3H_7OH$ . . .	1.7	Unlimited
Benzene, $C_6H_6$ . . . . .	0	0.057
Nitrobenzene, $C_6H_5NO_2$ . . .	4.19	0.19
Aniline, $C_6H_5NH_2$ . . . . .	1.51	3.49
Phenol, $C_6H_5OH$ . . . . .	1.70	8.2

12. There is, however, one group of dipoles for which dipole moment alone is quite insufficient to yield a guide to solubility relationships. The dipoles present in water, the alcohols, ammonia, organic amines, and hydrogen fluoride are attracted to each other by exceptionally strong forces. This is illustrated particularly in Fig. 4, where boiling points of certain series of compounds are plotted against molecular weights. For most of the compounds shown, the boiling point increases with increasing molecular weight, but water, hydrogen chloride and ammonia have much higher boiling points than would be expected on this basis. These liquids also freeze at abnormally high temperatures, forming solids having a peculiar type of structure. The structure of ice is indicated in Fig. 5. This is a comparatively open structure, with a density less than that of water. Each atom of oxygen is surrounded by four others, and atoms of hydrogen are on a line between the atoms of oxygen, although nearer one atom of oxygen than the other.

It follows that a substance, in order to be soluble in water, must be capable of tearing apart the so-called "**hydrogen bond**," and the substances here under discussion all readily mix with each other. Non-polar molecules, however, or even those containing ordinary dipoles, often fail

to penetrate the structure of water. Referring again to Table 3, we see that propyl alcohol has about the same dipole moment as propyl iodide and propyl bromide, but that whereas the latter two have very limited solubility in water, the first is completely miscible with water, due to the fact that its hydroxyl groups are able to take part in the structures appropriate to water. Again, in Table 3 we see the dipole moment and solubility in water of benzene and three other substituted products, nitrobenzene, aniline and phenol. The relative solubilities in water evidently have no relation to the dipole moment, but they do accord well with the ability to form hydrogen bonds with water, the  $\text{—OH}$  of phenol entering most readily into the structure and the  $\text{—NH}_2$  of aniline less readily. The nitro group of nitrobenzene, although it is the most polar of all, does not help a great deal in bringing nitrobenzene into solution in water.

**13. Electrolytes.** The nature of the process of solution of a salt was illustrated in Chapter V, Fig. 1. It is evident from this that the solubility of a salt is favored by high dielectric constant on the part of the solvent and water and ammonia are particularly effective. In order to compare the solubilities of different salts, let us break up the process of the solution of the solid in water into two steps: first, the separation of the ions of the solid crystal into gaseous ions, and then the hydration of these ions by bringing them separately into water.



Such a process is, of course, not easy to realize practically, but it is quite legitimate to consider it theoretically. The energy required for the first part of this process, that is, the separation of the solid ions into gaseous ions, is called the lattice energy of the substance. This process was one of the steps considered in Chapter V, Table 1. The amount of energy that must be put in for this step in the process



evidently depends, first, upon how close the solid ions are in the lattice; second, upon their charge; third, upon the nature of the ions themselves—for example, whether their kernels are surrounded by 8 or by some other number of electrons. Kernels with 18 electrons are, as it were, softer, more soluble, and can get closer to ions of the opposite charge than kernels containing fewer electrons. The energy recovered in the second stage of the process, the hydration of the gaseous ions, depends on the size and charge of the ions and the nature of the electron kernel. The same factors, therefore, tend both to assist the solubility in so far as the second step in the process is concerned, and to oppose it in the first. However, the different steps do not operate in quite the same way in the two cases, and the net result differs for different substances. It is obvious here, as in so many other cases of physico-chemical phenomena, that no extremely simple rules can be formulated. A few illustrations will show, however, the usefulness of the above scheme of analysis.

TABLE 4  
HYDRATION, SOLUBILITY AND IONIC SIZE FOR  
SULFATES OF THE TYPE,  $\text{MSO}_4$

ION	RADIUS $\times 10^8$ CM.	H <sub>2</sub> O IN SOLID	SOLUBILITY G. PER 100 G. H <sub>2</sub> O
$\text{SO}_4^{--}$	3.0	—	—
$\text{Ba}^{++}$	1.4	0	0.0002
$\text{Pb}^{++}$	1.3	0	0.004
$\text{Sr}^{++}$	1.15	0	0.01
$\text{Ca}^{++}$	1.0	2	0.2
$\text{Fe}^{++}$	0.8	7	21.
$\text{Mg}^{++}$	0.75	7	27.

14. In Table 4 are given the solubilities of a series of sulfates of doubly charged positive ions, together with the water of hydration of the solid crystal and the radii of the ions. The sulfate ion is of course larger than any of the positive ions with which it is combined. The smallest posi-

tive ion of the series,  $\text{Mg}^{++}$ , does not by itself fill up very well the space between the sulfate ions, and there is room for 7 molecules of water around each magnesium ion. Even in the solid state, the magnesium sulfate is already largely hydrated and it is an easy process for the ions to be further separated on going into solution; that is, the substance is very soluble in water. As the size of the positive ion increases, however, in going finally to barium ion,  $\text{Ba}^{++}$ , we arrive at a substance whose two ions have more nearly equal size and which can pack firmly into a solid crystal, with no need for water to fill it out. The result is an extremely insoluble substance.

TABLE 5

SUBSTANCE	IONS	RADII $\times 10^8$ CM.	SOLUBILITY G. PER 100 G. $\text{H}_2\text{O}$
NaCl	$\text{Na}^+$ , $\text{Cl}^-$	1.0, 1.8	24
CuS	$\text{Cu}^{++}$ , $\text{S}^{--}$	1.0, 1.8	0.00003

15. The combined effect of ionic charge and 18-electron kernel is illustrated in Table 5, comparing NaCl and CuS, both of which have the same crystal structure and practically the same ionic radii. The greater attraction of the ions of CuS for each other is attributable, first, to their double charge, which, according to Coulomb's law, means 4 times the interionic attraction at equal distances; second, to the greater interaction of the larger number of electrons. The greater strength of hydration, due to these same causes, evidently is not sufficient to offset the large lattice energy.

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# Appendix

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## *Sample Final Examination Questions for the First Semester*

1. Which solution in the following list

- |   |  |   |
|---|--|---|
| (a) 0.01 M-HCl                            | (e) 0.01 M-NaCl  | (h) 0.1 M-NaHCO <sub>3</sub>              |
| (b) 0.5 M-Na <sub>2</sub> CO <sub>3</sub> | (f) 0.001 M-KOH  | (i) 0.01 M-H <sub>2</sub> SO <sub>4</sub> |
| (c) 0.001 M-Ba(OH) <sub>2</sub>           | (g) 0.01 M-(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> | (j) 0.5 M-NaOH                            |
| (d) 0.01 M-NH <sub>3</sub>                |  |   |

has a molal concentration of OH<sup>-</sup> nearest to (indicate by writing the corresponding letter)

- |                       |                      |                       |
|-----------------------|----------------------|-----------------------|
| (1) 10 <sup>-2</sup>  | (4) 10 <sup>-8</sup> | (7) 10 <sup>-13</sup> |
| (2) 10 <sup>-3</sup>  | (5) 10 <sup>-6</sup> |                       |
| (3) 10 <sup>-11</sup> | (6) 10 <sup>-7</sup> |                       |

2. The atoms R, X, Y and Z have, respectively, one, two, two and seven valence electrons. Their atomic numbers increase in the order, X, Y, Z, R. Atoms X and R have 8 electrons immediately below their valence electrons and atoms Y and Z have 18. Which are atoms of metallic elements?..... Write the formula of the simplest ion of Z .....; of X.....; of the complex ammonia ion most likely to form.....; of the hydroxide that is the strongest base.....; of a probable compound between X and Z.....
3. 0.2 mole of BaCO<sub>3</sub> weighs.....grams; will give.....grams, or.....moles of CO<sub>2</sub> gas. This gas will occupy.....liters at 273° C. and 0.2 atmosphere. The BaO left on strongly heating the 0.2 mole of BaCO<sub>3</sub> will react with 5 liters of water to give.....molal or.....normal Ba(OH)<sub>2</sub>. The concentration of OH<sup>-</sup> in this solution will be ..... molal. 100 cc. of this solution will neutralize ..... cc. of 0.5 M-HCl.
4. If the hypothetical ion, M<sup>+</sup>, shows the following reactions:  
(a) MCl + Na<sub>2</sub>CO<sub>3</sub> (aq.) gives a ppt. which, after filtration, easily dissolves in HNO<sub>3</sub> (aq.).

(b)  $M_2SO_4$  dissolves in KCN (aq.).

(c)  $M_2SO_4$  ppt. +  $H_2S$  gives  $M_2S$  ppt.

(d) The product obtained on treating  $M_2SO_4$  with  $Na_2CO_3$  (aq.) and filtering out is insoluble in  $HNO_3$  (aq.).

State, in words, two reactions that you can predict with certainty from these observations.

5. State the effect, quantitatively where you can, of each of the following changes upon (a) the number of molecular impacts per second per square centimeter upon the containing walls and (b) the force of each impact.

(1) Gas in a cylinder with a movable piston, immersed in a large water bath, is compressed from 3 liters to 2 liters.

Ans. (a) ..... (b) .....

(2) The air pressure in an automobile tire is slowly pumped up from 25 lbs. per sq. in. to 30 lbs. per sq. in.

Ans. (a) ..... (b) .....

(3)  $H_2S$  gas is kept in a closed vessel at constant temperature until it has all decomposed into  $H_2$  and liquid sulfur.

Ans. (a) ..... (b) .....

6. Which of the substances,  $NaOH$ ,  $Al_2O_3$ ,  $Al_2(SO_4)_3$ ,  $CaSO_4 \cdot 2H_2O$ ,  $Na_2CO_3$ ,  $K_2SO_4$ ,  $ZnS$ ,  $ZnSO_4$ ,  $Na_2B_4O_7$ ,  $CaCl_2$ ,  $CaSO_4 \cdot \frac{1}{2}H_2O$ ,  $MgO$ ,  $CaSO_4$ ,  $(NH_4)_2SO_4$ , is most appropriate for each of the following uses:

(1) Water softener. .... (5) Cleaning metals for welding

(2) White paint. .... or hard soldering. ....

(3) Abrasive. .... (6) Making plaster casts. ....

(4) Making soap from fat. .... (7) Fertilizer. ....

(8) Avoiding dust on roads. ....

7. Give the formulas of the solids remaining after evaporating to dryness solutions of the following:

(1) 0.1 mole  $AgCl$  and 1 mole  $HNO_3$ . ....

(2) 0.02 mole  $NH_4Cl$  and 0.05 mole of  $NaOH$ . ....

(3) 0.02 mole  $Zn(NO_3)_2$  and 1 mole  $HCl$ . ....

(4) 0.1 mole  $Zn(NO_3)_2$  and 0.01 mole  $H_2SO_4$ . ....

(5) 0.02 mole  $CuSO_4$  and 0.2 mole  $HNO_3$ . ....

8. Given that the elements  $A$ ,  $B$ ,  $C$ ,  $D$  and  $E$  have atomic numbers (nuclear charges) of 6, 9, 13, 19 and 30 respectively, underline correct answers below.

(a) The compound of  $A$  and  $B$  will have the formula  $AB$ ,  $AB_2$ ,  $A_2B$ ,  $AB_4$ ,  $A_4B$ .

(b) Which of the following complex ions are stable?  $C(NH_3)_4^{++}$ ,  $D(NH_3)_2^+$ ,  $E(NH_3)_6^{+++}$ ,  $E(NH_3)_4^{++}$ .

- (c) Which of the elements are ordinarily gases with diatomic molecules? *A, B, C, D, E.*
- (d) The compound of *B* and *D* will be essentially ionic, electron pair bonded.
- (e) Which of the elements are metals? *A, B, C, D, E.*
- (f) The compound of *B* and *C* will have the formula *CB, CB<sub>2</sub>, CB<sub>3</sub>, CB<sub>4</sub>, C<sub>4</sub>B, C<sub>2</sub>B.*

9. Which solution in the following list:

- |   |                                |                            |
|---|--------------------------------|----------------------------|
| (a) 0.1 M-HAc                             | (d) 0.05 M-Ba(OH) <sub>2</sub> | (g) 1 M-NH <sub>4</sub> Ac |
| (b) 1 M-NaAc                              | (e) 1 M-NaOH                   | (h) 1 M-HCl                |
| (c) 0.5 M-Na <sub>2</sub> CO <sub>3</sub> | (f) 0.1 M-HCl                  |                            |

has a molal concentration of OH<sup>-</sup> nearest to (indicate by writing the corresponding letter)

- |                            |                             |
|----------------------------|-----------------------------|
| (1) 10 <sup>-7</sup> ..... | (3) 10 <sup>-5</sup> .....  |
| (2) 10 <sup>-1</sup> ..... | (4) 10 <sup>-11</sup> ..... |

10. Underline the formula of that substance in each of the following groups which has the property stated in the highest degree:

- |  |  |
|--|--|
| (a) Solubility in water:                                 | CaCO <sub>3</sub> , BaSO <sub>4</sub> , CaSO <sub>4</sub> , CaC <sub>2</sub> O <sub>4</sub>  |
| (b) Density (all gases):                                 | N <sub>2</sub> O, H <sub>2</sub> , NH <sub>3</sub> , C <sub>2</sub> H <sub>6</sub>   |
| (c) Conc. of OH <sup>-</sup> :                           | 0.5 M-Na <sub>2</sub> CO <sub>3</sub> , 1 M-NaHCO <sub>3</sub> ,<br>0.05 M-Ba(OH) <sub>2</sub> , 1 M-NH <sub>4</sub> -<br>OH, 0.05 M-KOH |
| (d) Conc. of H <sup>+</sup> :                            | 0.01 M-H <sub>2</sub> SO <sub>4</sub> , 1 M-HAc, 1<br>M-NH <sub>4</sub> NO <sub>3</sub> , 0.04 M-HCl                                     |
| (e) Atomic number:                                       | K, Mg, Al, Li, Ag, Cu  |
| (f) Acidic nature:                                       | Zn(OH) <sub>2</sub> , Cu(OH) <sub>2</sub> , Ca(OH) <sub>2</sub> ,<br>LiOH  |
| (g) Degree of hydrolysis:                                | 0.1 M-KAc, 0.1 M-NH <sub>4</sub> Ac,<br>0.1 M-NH <sub>4</sub> NO <sub>3</sub>  |
| (h) Effect on the freezing point<br>of 1 liter of water: | 0.02 mole of KCl, 0.01 mole of<br>K <sub>2</sub> SO <sub>4</sub> , 0.03 mole of HAc,<br>0.01 mole of BaCl <sub>2</sub>                   |
| (i) Ionizing potential of the<br>gaseous atom:           | Na, Ca, Al, Ag<br>CaSO <sub>4</sub> , Ca(OH) <sub>2</sub> , CaC <sub>2</sub> O <sub>4</sub> ,  |
| (j) Insolubility in water:                               | Ca(NO <sub>3</sub> ) <sub>2</sub>  |

11. Some solid Ca(OH)<sub>2</sub> is in equilibrium with its saturated solution. How will the amount of solid Ca(OH)<sub>2</sub> be affected (indicate by writing +, - or 0 for increase, decrease or practically no effect, respectively) by adding small amounts of the following:

- |                                      |                           |   |
|--------------------------------------|---------------------------|---|
| (a) KOH.....                         | (d) HAc.....              | (g) $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ..... |
| (b) $\text{Ca}(\text{NO}_3)_2$ ..... | (e) $\text{CaCO}_3$ ..... | (h) $\text{ZnSO}_4$ .....                       |
| (c) $\text{NH}_4\text{Cl}$ .....     | (f) $\text{KNO}_3$ .....  |   |

12. Give the concentration of  $\text{OH}^-$  in each of the following solutions as accurately as you can. Some latitude will be allowed in certain cases:

- |  |   |
|--|---|
| (a) 1 M- $\text{NH}_4\text{OH}$ .....        | $\text{Ba}(\text{OH})_2$ and 100 cc. of |
| (b) 0.01 M- $\text{NH}_4\text{OH}$ .....     | 0.05 M-HCl .....                        |
| (c) 0.5 M- $\text{Na}_2\text{CO}_3$ .....    | (h) A molal solution of the so-         |
| (d) 0.01 M- $\text{NH}_4\text{Ac}$ .....     | dium salt of an acid                    |
| (e) $\text{CO}_2$ at 1 atm.....              | whose degree of dissocia-               |
| (f) Saturated $\text{Ca}(\text{OH})_2$ ..... | tion is 0.01 of that of                 |
| (g) A solution resulting from                | HAc when both are in                    |
| mixing 100 cc. of 0.1 M-                     | molal solution.....                     |

13. The following are mixed in 1 liter of water in the order given. Write the formula of the precipitate finally present. 0.05 mole of  $\text{CaCl}_2$ , 1 mole of  $\text{HCl}$ , 0.1 mole of  $\text{Na}_2\text{SO}_4$ , 0.1 mole of  $\text{NH}_3$ , 0.2 mole of  $\text{Na}_2\text{CO}_3$ .  
*Ans.*.....

## *Sample Final Examination Questions for the Second Semester*

Questions 1-4 represent hypothetical "unknowns," made by selecting one or more of the substances listed in each case. The amounts are not necessarily equivalent but are always more than mere traces.

On the basis of the observations given, write, in the space immediately following the formula, + for each substance known to be present, - for each substance known to be absent, and a question mark (?) for each substance whose presence is in doubt.

- |                                     |  |
|-------------------------------------|--|
| 1. $\text{Pb}(\text{NO}_3)_2$ ..... | Treatment with hot water gives a       |
| $\text{CuSO}_4$ .....               | white residue and a colorless solu-    |
| $\text{HgCl}_2$ .....               | tion, which, after filtration, gives a |
| $\text{ZnCl}_2$ .....               | white ppt. on addition of ammonia,     |
| $(\text{NH}_4)_2\text{SO}_4$ .....  | insoluble in excess.                   |
| $\text{K}_2\text{CrO}_4$ .....      |  |
| $\text{NaNO}_3$ .....               |  |



2. Zn..... Treatment with 0.1 M- $\text{H}_2\text{SO}_4$  gives effervescence, and leaves a residue, which, after separation from the solution, dissolves in 2 M- $\text{HNO}_3$  to give a colorless solution. The sulfuric acid solution gives no ppt. on addition of  $\text{H}_2\text{S}$  but a black ppt. upon subsequent addition of  $\text{NaOH}$ .  
 Cu.....  
 Ag.....  
 Fe.....  
 Al.....
3.  $\text{SnCl}_2$ ..... Treatment with water gives a green solution and leaves a white residue, which is filtered out. The green solution, upon addition of 6 M- $\text{NaOH}$ , gives a ppt., soluble in excess. The white residue is not visibly affected by ammonia.  
 $\text{Fe}_2(\text{SO}_4)_3$ .....  
 $\text{KHSO}_4$ .....  
 $\text{K}_2\text{Cr}_2\text{O}_7$ .....  
 $\text{Hg}_2\text{Cl}_2$ .....  
 $\text{FeSO}_4$ .....  
 $\text{Ba}(\text{NO}_3)_2$ .....  
 $\text{ZnCl}_2$ .....
4.  $\text{K}_2\text{SO}_4$ ..... Treatment with 0.3 M- $\text{HCl}$  gives a solution and a dark gray residue which is filtered out. The solution, upon addition of ammonia, remains colorless, but gives a white ppt. The dark gray residue turned white and partly dissolved when treated with hot 2 M- $\text{HNO}_3$ . This white residue is insoluble in 6 M- $\text{NaOH}$ .  
 $\text{ZnS}$ .....  
 $\text{Al}_2\text{O}(\text{OH})_4$ .....  
 $\text{BaCO}_3$ .....  
 $\text{CuO}$ .....  
 $\text{HgCl}_2$ .....  
 $\text{Pb}(\text{NO}_3)_2$ .....
5. Answer the following by underlining the symbol or formula of the substance having the characteristic called for:
- (1) The highest melting point Fe, Zn, W, Ni, Bi  
 (2) The greatest hardness  $\text{SnO}_2$ ,  $\text{SiO}_2$ ,  $\text{PbO}_2$ ,  $\text{SO}_2$   
 (3) The greatest affinity for electrons  $\text{Cl}_2$ ,  $\text{Fe}^{+++}$ ,  $\text{H}^+$ ,  $\text{I}_2$ , Zn  
 (4) The largest number of valence electrons Sb, Sn, Si, Al, Ag  
 (5) The highest oxidation number of vanadium  $\text{VO}^{++}$ ,  $\text{NH}_4\text{VO}_3$ ,  $\text{V}_2(\text{SO}_4)_3$ ,  $\text{VS}_2$ ,  $\text{V}(\text{CN})_6^{----}$   
 (6) The largest degree of hydrolysis  $\text{KAsO}_3$ ,  $\text{KPO}_3$ ,  $\text{KNO}_3$ ,  $\text{KNO}_2$ ,  $\text{KAsO}_2$   
 (7) The largest atomic number B, Br, Ba, Bi  
 (8) The largest solubility in water  $\text{HgS}$ ,  $\text{CuS}$ ,  $\text{FeS}$ ,  $\text{PbS}$ ,  $\text{SnS}$

6. State the colors of the following:

- |                                   |  |  |
|-----------------------------------|--|--|
| (1) $\text{Fe}_2\text{O}_3$ ..... | (6) $\text{HgS}$ .....                 | (11) $\text{I}_2$ vapor.....                   |
| (2) $\text{Cr}_2\text{O}_3$ ..... | (7) $\text{Cr}_2\text{O}_7^{--}$ ..... | (12) $\text{Cu}^{++}$ .....                    |
| (3) $\text{Al}_2\text{O}_3$ ..... | (8) $\text{Fe}^{++}$ .....             | (13) $\text{Fe}_2\text{Fe}(\text{CN})_6$ ..... |
| (4) $\text{Pb}_3\text{O}_4$ ..... | (9) $\text{Fe}^{+++}$ .....            | (14) $\text{PbO}_2$ .....                      |
| (5) $\text{PbCrO}_4$ .....        | (10) $\text{Cl}_2$ .....               | (15) $\text{CoSiO}_3$ .....                    |

7. Underline the two substances in each of the following series which most closely resemble each other in chemical behavior:

- |   |   |
|---|---|
| (1) $\text{Al}^{+++}$ , $\text{Bi}^{+++}$ , $\text{Cr}^{+++}$ , $\text{Fe}^{+++}$ | (4) $\text{SO}_4^{--}$ , $\text{ClO}_4^-$ , $\text{SiO}_4^{--}$ , $\text{CrO}_4^{--}$ |
| (2) $\text{BaO}_2$ , $\text{SO}_2$ , $\text{MnO}_2$ , $\text{PbO}_2$              | (5) $\text{HgS}$ , $\text{PbS}$ , $\text{FeS}$ , $\text{ZnS}$                         |
| (3) $\text{K}^+$ , $\text{Ag}^+$ , $\text{Hg}_2^{++}$ , $\text{Cu}^{++}$          |   |

8. Answer the following by underlining the substance having the characteristic called for:

The greatest hardness	$\text{MgO}$ , $\text{As}_2\text{O}_3$ , $\text{Al}_2\text{O}_3$ , $\text{CaO}$
The greatest affinity for electrons	$\text{Ag}^+$ , $\text{Hg}^{++}$ , $\text{Cl}_2$ , $\text{Br}_2$ , $\text{Fe}^{+++}$
The largest number of valence electrons	$\text{Br}$ , $\text{B}$ , $\text{Ba}$ , $\text{Bi}$ , $\text{Be}$
The highest atomic number	$\text{Ag}$ , $\text{Hg}$ , $\text{Mg}$ , $\text{Mn}$ , $\text{Al}$
The lowest oxidation number of molybdenum	$\text{Na}_2\text{MoO}_4$ , $\text{MoF}_6$ , $\text{Mo}_3\text{O}_8$ , $\text{Mo}(\text{OH})_3$ , $\text{MoS}_2$ , $\text{MoO}_3$
The largest atomic radius	$\text{Na}$ , $\text{Cr}$ , $\text{Ca}$ , $\text{K}$ , $\text{Br}$
The lowest melting point	$\text{C}$ , $\text{Si}$ , $\text{Ni}$ , $\text{Fe}$ , $\text{Sn}$
The strongest reducing power	$\text{I}^-$ , $\text{F}^-$ , $\text{Cl}^-$ , $\text{Br}^-$

9. An electric cell consists of an electrode of silver coated with silver chloride, and another of zinc, both immersed in a solution of 0.01 M- $\text{ZnCl}_2$ .

As the cell discharges, electrons flow in the external circuit from the ..... electrode. The oxidizing agent is ..... and the reducing agent is ..... The half-reaction occurring at the silver-silver chloride electrode is ..... If the concentration of the  $\text{ZnCl}_2$  were increased the electromotive force of the cell would be ..... The cell evolves heat while discharging, hence the electromotive force would be ..... by lowering the temperature.

10. How many moles of each of the following oxidizing agents would be required to oxidize 0.1 mole of  $\text{Ti}^{+++}$  to  $\text{TiO}^{++}$  and how many moles of  $\text{H}^+$  would be used (denote by  $-$ ), or liberated (denote by  $+$ ), in each case.

Oxidizing agent	$\text{Fe}^{+++}$	$\text{Hg}_2^{++}$	$\text{Cl}_2$	$\text{MnO}_4^-$ to $\text{Mn}^{++}$
No. of moles . . . . .				
No. of moles of $\text{H}^+$ . . . . .				

11. The atoms X, Y and Z have atomic weights increasing in that order. X has 2, 8, 8, 2 electrons outside its nucleus. The atomic number of Y is 11 greater than that of X and the atomic number of Z is 15 greater than that of X. The simplest ions of these elements are . . . . .  
The strongest reducing agent is . . . . . The least metallic element is . . . . .

Questions 12–15 represent “unknowns” made by selecting one or more of the substances listed in each case. The amounts are not necessarily equivalent but are always more than mere traces. Mark + for those known to be present, – for those known to be absent, and ? for those which are undetermined.

- |   |  |
|---|--|
| 12. $\text{KHSO}_4$ . . . . .           | The unknown dissolves in water to give a clear orange colored solution.  |
| $\text{Pb}(\text{NO}_3)_2$ . . . . .    |  |
| $\text{NaNO}_3$ . . . . .               |  |
| $(\text{NH}_4)_2\text{CrO}_4$ . . . . . |  |
| $\text{BaCO}_3$ . . . . .               |  |
| $\text{KCl}$ . . . . .                  |  |
| 13. $\text{AgNO}_3$ . . . . .           | The unknown is partially soluble in water, but leaves a white residue. When the residue is treated with $\text{NH}_4\text{OH}$ , a solution and a black residue are obtained. Acidifying the ammoniacal solution with 1 M- $\text{HNO}_3$ gives a white precipitate. The gradual addition of $\text{NaOH}$ solution to the original aqueous solution gives a white precipitate insoluble in excess $\text{NaOH}$ solution. |
| $\text{Hg}_2\text{Cl}_2$ . . . . .      |  |
| $\text{KNO}_3$ . . . . .                |  |
| $\text{NH}_4\text{Cl}$ . . . . .        |  |
| $\text{Na}_2\text{SO}_4$ . . . . .      |  |
| $\text{HgCl}_2$ . . . . .               |  |
| 14. $\text{HgCl}_2$ . . . . .           | Treatment with hot water yields a grayish brown residue and a yellow solution. With conc. $\text{HCl}$ the precipitate effervesces, and on heating gives a pungent gas and a clear solution. One portion of the original aqueous solution turned orange without effervescing on the addition of dil. $\text{HCl}$ . The other portion of it gave a white precipitate and finally   |
| $\text{PbO}_2$ . . . . .                |  |
| $\text{ZnSO}_4$ . . . . .               |  |
| $\text{K}_2\text{CrO}_4$ . . . . .      |  |
| $\text{BaCl}_2$ . . . . .               |  |
| $\text{CaCO}_3$ . . . . .               |  |
| $\text{NaNO}_3$ . . . . .               |  |

a solution on the gradual addition of .1 M-NaOH.

15. FeS..... The unknown is partially soluble in cold water. When the residue is treated with 6 M-NaOH, a green solution is obtained, and a dark residue which dissolves in 1 M-HCl with effervescence. The addition of NaAc and Na<sub>2</sub>CrO<sub>4</sub> solution to the boiled HCl solution gives a yellow precipitate. The original aqueous solution imparts a violet color to the flame which can be seen without the use of a cobalt glass. The addition of NaOH to this solution gave no odor.
- Cr(OH)<sub>3</sub>.....
- BaCO<sub>3</sub>.....
- NaCl.....
- KNO<sub>3</sub>.....
- NH<sub>4</sub>Cl.....

16. What is the color of (1) SnS..... (2) PbCrO<sub>4</sub>.....  
(3) HgNH<sub>2</sub>Cl..... (4) Fe<sub>2</sub>Fe(CN)<sub>6</sub>..... (5) Fe(OH)<sub>3</sub>.....

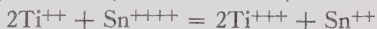
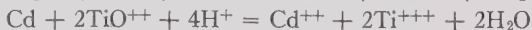
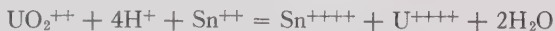
17. Which solvent in the following list:

(a) CS<sub>2</sub>, (b) Cl<sub>2</sub>(aq.), (c) 6 M-NH<sub>4</sub>OH, (d) 6 M-NaOH,  
(e) 0.3 M-HCl, (f) 0.3 N-H<sub>2</sub>SO<sub>4</sub>, (g) NH<sub>4</sub>SH(aq.)

would be most effective in dissolving (answer each simply by writing in the corresponding letter from the above list)

- (1) PbSO<sub>4</sub>..... (5) BaCrO<sub>4</sub>.....  
(2) AgCl..... (6) CaC<sub>2</sub>O<sub>4</sub>.....  
(3) Hg<sub>2</sub>Cl<sub>2</sub>..... (7) SnS<sub>2</sub>.....  
(4) Sulfur..... (8) CuHAsO<sub>3</sub>.....

18. The following reactions are observed, using 0.1 molal solutions and approximately equivalent amounts:



On the basis of these observations, select (1) the strongest oxidizing agent, ....., (2) the strongest reducing agent, ..... If the data are insufficient to permit a decision, write in the word "undetermined."

Questions 19, 20, 21 and 22 represent hypothetical "unknowns" made by selecting one or more of the substances listed in each case. The amounts are not necessarily equivalent but are always more than mere traces. On the basis of the observations given, mark — all substances known to be absent, mark + those known to be present, and mark ? those whose presence is in doubt.

19.  $\text{BaCO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{CaCl}_2$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{KOH}$

Treatment with water gives a white residue, A, and a solution, B. The residue, A, filtered out and washed, is insoluble in dilute  $\text{HCl}$ . The solution, B, shows a violet flame test without using cobalt glass, and upon treatment with dilute  $\text{HCl}$  it gives effervescence, and a white ppt. soluble in excess of the acid.

20.  $\text{ZnS}$ ,  $\text{PbCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{CrCl}_3$ ,  $\text{KHSO}_4$ ,  $\text{HgS}$

Treatment with 0.3 M- $\text{HCl}$  gives a black ppt., A, and a solution, B. The ppt., A, after filtration and washing, dissolves in hot 2 M- $\text{HNO}_3$ , except for a small dirty yellow residue. The solution, B, treated with excess of 6 M- $\text{NaOH}$ , gives a green solution and no ppt.

21.  $\text{AlCl}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{CaO}$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  
 $\text{CuSO}_4$ ,  $\text{SnCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$

Treatment with water gives an odorless, yellow solution, and a white ppt., which, after filtration and washing, is not visibly affected by either  $\text{H}_2\text{S}$  or  $\text{NH}_3$ .

22.  $\text{Zn}$ ,  $\text{Sn}$ ,  $\text{Fe}$ ,  $\text{Hg}$ ,  $\text{Ag}$ ,  $\text{PbO}_2$

When treated with hot 2 M- $\text{HCl}$ , the unknown gives a pungent gas, a yellow solution and a white residue. The yellow solution yields a black ppt. on passing in  $\text{H}_2\text{S}$ .

23. Atom X has an atomic number of 10. Atom Y has 7 valence electrons, with 2 electrons in the group below the valence group. Atom Z has 11 more extra nuclear electrons than Y. Atom Q has 2 valence electrons, with 18 in the underlying level. On the basis of these figures, supply the following information. The formula of: (a) the most stable ion of Y . . . . ., (b) of Z . . . . ., (c) the molecule of the free element X . . . . ., (d) the molecule of the element Y . . . . ., (e) the most basic hydroxide . . . . ., (f) the most stable binary compound with hydrogen . . . . ., (g) the most probable ammonia complex ion . . . . ., (h) the hydroxide most likely to be amphoteric . . . . .

24. Which solvent in the following list:

(a) 0.3 N- $\text{H}_2\text{SO}_4$  (c) 6 M- $\text{NaOH}$  (e)  $\text{CCl}_4$  (g)  $\text{Br}_2(\text{aq.})$   
(b) 0.3 N- $\text{HCl}$  (d) 6 M- $\text{NH}_4\text{OH}$  (f)  $\text{NH}_4\text{SH}(\text{aq.})$

would be most effective (answer by writing only the letter, *a*, *b*, *c*, etc.) for dissolving each of the following

- (1)  $\text{CaC}_2\text{O}_4$ ..... (4)  $\text{PbCrO}_4$ ..... (7)  $\text{C}_{24}\text{H}_{50}$ .....  
 (2)  $\text{Ag}_2\text{CO}_3$ ..... (5)  $\text{HgS}$ ..... (8)  $\text{Hg}_2\text{Br}_2$ .....  
 (3)  $\text{HgO}$ ..... (6)  $\text{SnS}_2$ ..... (9)  $\text{Pb}(\text{OH})_2$ .....

25. How many valence electrons are there in each of the following?

- (1)  $\text{Na}$ ..... (4)  $\text{Cl}^-$ ..... (7)  $\text{NH}_3$ ..... (10)  $\text{SO}_4^{--}$ .....  
 (2)  $\text{H}^+$ ..... (5)  $\text{F}_2$ ..... (8)  $\text{NH}_4^+$ .....  
 (3)  $\text{H}_2$ ..... (6)  $\text{HCl}$ ..... (9)  $\text{CaO}$ .....

26. 112 cc. of  $\text{Cl}_2$  at 1 atmosphere and  $0^\circ$  is passed into 100 cc. of 0.2 M- $\text{FeCl}_2$ . Supply the numbers called for in the following table.

	Before passing in $\text{Cl}_2$		After passing in $\text{Cl}_2$	
	No. of moles	Conc.	No. of moles	Conc.
$\text{Fe}^{++}$	.....	.....	.....	.....
$\text{Fe}^{+++}$	.....	.....	.....	.....
$\text{Cl}^-$	.....	.....	.....	.....
$\text{Cl}_2$	.....	..... in gas	.....	.....

27. An electric cell consists of an electrode of platinum in contact with gaseous hydrogen and another of  $\text{PbO}_2$ , both electrodes dipping into 0.1 M- $\text{H}_2\text{SO}_4$ . Write equations for

- (a) The reaction at the hydrogen electrode.....  
 (b) The reaction at the  $\text{PbO}_2$  electrode.....  
 (c) The total cell reaction.....

The voltage of the cell would be increased, decreased, unaffected by  
 (cross out two)

substituting 0.2 M- $\text{H}_2\text{SO}_4$ . The oxidizing agent is ....., the  
 reducing agent is .....



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REFERENCE BOOK  
*of Inorganic  
Chemistry*

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BY WENDELL M. LATIMER

Professor of Chemistry in the University of California

AND JOEL H. HILDEBRAND

Professor of Chemistry in the University of California

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## PREFACE TO THE REVISED EDITION

We have sought in this revision to extend the usefulness of the book as a general reference in the field of inorganic chemistry. In order to provide a convenient single volume to which the chemist may turn to find the facts or data relevant to the majority of problems which he may encounter, it has been necessary to carefully select the material. Thermodynamical data, such as oxidation potentials, equilibrium constants, and free energies, may be used to express so concisely the tendency for a reaction to occur and the nature of the equilibrium state, that this side of the book has been enlarged to include practically all of the available data pertaining to aqueous solutions. The recent developments in atomic, molecular, and crystal structure, atomic sizes, bond distances and bond energies have contributed much to the correlation of inorganic chemistry and we have included the more important facts in this field. The chapter on the atomic nucleus has been completely rewritten in line with the discoveries which have been made during the past ten years in nuclear physics. New investigations have been noted in the general field of chemical facts, and many of the older values for the physical constants of inorganic substances have been revised. Sections dealing with the chemical industries have been brought up to date, and a considerable extension has been made in the treatment of the organic chemical industries.

The text has not been "written down" to the level of elementary students. A foreign language may be mastered either by starting with a primer or by hearing the language spoken and used in every day life. In the first year chemistry course at the University of California, both methods of teaching the language of chemistry are employed. We

believe that, by the end of the year, the students can acquire the facility to read and understand the Reference Book, and that this ability to read chemical literature should be a most important factor in his development.

W. M. L.

J. H. H.

BERKELEY, CALIFORNIA  
January, 1940.

## PREFACE TO THE FIRST EDITION

This book represents the fulfillment of a plan, long cherished, of providing a volume of descriptive chemistry to complete the series begun with "Principles of Chemistry" by Hildebrand, which adheres strictly to its title, and continued with the "Course in General Chemistry" by Bray and Latimer, which presents a laboratory course. The rather radical experiment in teaching general chemistry, begun in the University of California in 1912, has been somewhat hampered by the lack of a reference book on descriptive chemistry employing the language and the point of view adopted for our instructional scheme.

This "Reference Book of Inorganic Chemistry" has been written as a reference book rather than a text. The authors have sought to present essential chemical facts briefly, clearly, and in due relation to other facts and principles. The instructor using it will have to map out his own course, following whatever order of arrangement appeals to him. The numbering of paragraphs will make it possible for him to assign for study material selected from any desired portion of the book. We feel that many teachers will welcome the greater freedom thus afforded of developing their own pedagogical methods.

Chemical properties have been widely related to atomic structures and sizes. These ideas, although new, and subject to revision, are so illuminating that they appeal strongly to the imagination. Moreover, they are not difficult to grasp; many concepts traditionally introduced into freshman courses are far more elusive.

The formulas of many compounds have been given in terms of the Lewis theory of valence, not with the idea that these formulas represent the definite locations of the

electrons, but rather to call attention to the importance of considering the total number of electrons or electron pairs in a molecule.

The extensive tabulation of "half reaction" potentials, equivalent to free energy values, will enable one to predict the direction and driving force of an immense number of reactions. Many of these potentials have been calculated for this book from reaction heats and entropy values, and have not heretofore been published.

We have treated industrial processes with emphasis upon their chemistry, relation to other industries, and economic magnitude, rather than upon their mechanical features. Illustrations of industrial processes, of the sort extensively used in some texts, have been left to the instructor to provide, as he can do so far more adequately, by the use of lantern slides and motion pictures. Many excellent films are now available at a nominal expense.

The book contains much more material than the average student, or even the average chemist, can assimilate. We believe, however, that students should be "exposed" to a far greater range of subject matter than is usually presented. We have found the appetite and assimilative capacity of the superior students to be almost unlimited, and we see no value in an intellectual diet list. For the average student, the presence of this extra material in the book does no more damage than the unordered articles listed on a restaurant menu.

We anticipate that this kind of a book will prove useful, not only to the freshman student, but also to the student who desires a reference book in advanced courses in chemistry and allied subjects; and further that teachers and industrial chemists will also find in it answers to many of their questions. To increase its usefulness, a large mass of data has been included in the form of tables, both in the text and in the various appendices.

In the endeavor to keep the size and cost of the book at



a low figure, it was decided to omit references to the original sources of material, although in many instances such references would be of historical and scientific value. Frequent use has been made of the more comprehensive treatises, especially: Gmelin-Kraut's *Handbuch der anorganischen Chemie*; Abegg and Auerbach *Handbuch der anorganischen Chemie*; *A Text-Book of Inorganic Chemistry*, Edited by Friend; *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* by Mellor; *Lexikon der anorganischen Verbindungen* by Hoffman; *Landolt-Börnstein Tabellen*; and *The International Critical Tables*.

The authors are much indebted to their colleagues in the Department of Chemistry of the University of California, especially to Professors G. N. Lewis and W. C. Bray, not only for specific criticisms and suggestions, but for many of the general ideas upon which our interpretation of the facts of inorganic chemistry has been constructed.

WENDELL M. LATIMER

JOEL H. HILDEBRAND

BERKELEY, CALIFORNIA  
December, 1928.



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Reference Book of  
Inorganic Chemistry





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# Chapter I

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## HYDROGEN

**1. Structure of Hydrogen Atom.**—The element, hydrogen, has three **isotopes**, their mass numbers being one, two, and three. The isotope of mass one is by far the most abundant; the hydrogen of ordinary water contains one part in seven thousand (approximately) of the isotope with mass two, and practically none of the isotope with mass three. The latter is formed in certain nuclear reactions but undergoes radioactive decomposition. The mass two isotope is called deuterium. This is the only case in which an isotope is designated by special name, but the percentage difference in the masses of hydrogen and deuterium greatly exceeds that of any two isotopes of the other elements and there is a correspondingly greater divergence in their physical and chemical properties.

The hydrogen atom (mass one isotope) is composed of two corpuscles; one, the **proton**, is positively charged and the other, the **electron**, is negatively charged. The mass of the proton is about 1,850 times that of the electron but the electrical charges, though opposite in sign, are equal in magnitude.

The atom has a large number of energy states representing different configurations of the electron and proton. The values for the energy of the atom in these different states may be expressed as a close approximation by the very simple relation,  $E = \frac{-13.54Z^2}{N^2}$  volts per unit charge, where

$Z$  is the charge on the proton (equal to unity) and  $N$ , called the **quantum number**, is any integer from 1 to  $\infty$ . The normal atom is in the first quantum state ( $N = 1$ ) and the energy in volts required to move the electron to the 2, 3, 4, 5,  $\dots \infty$  quantum states is shown in Fig. 1. When  $N = \infty$  the energy is zero. This corresponds to the complete separation of the electron and proton, and the total energy required per unit charge is given as 13.54 volts.

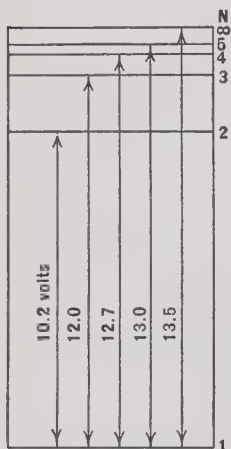


FIG. 1. Energy levels in the hydrogen atom.

When the electron moves from a higher quantum level to a lower, the energy difference is emitted in the form of light, whose frequency,  $\nu$ , is related to the energy difference,  $\Delta E$ , by the equation,  $\Delta E = h\nu$ , where  $h$  is a constant ("Planck constant"). Likewise the atom in a lower quantum state may absorb energy in the form of light of a given frequency and the electron thereby move to a quantum level of correspondingly higher energy. The spectral lines arising from electrons falling from outer levels to the first quantum level are far

out in the ultraviolet, but transitions from outer levels to the second quantum state give rise to the Balmer series which is in the visible spectrum. The highest frequency in the hydrogen spectrum is, of course, that corresponding to the electron falling from the infinite quantum state.

Bohr has sought to account for these quantum states by picturing the electron as revolving about the proton in some one of a number of possible orbits, which are circles or ellipses. These orbits are defined by the restriction that the momentum of the system must always be some multiple, i.e. the quantum number, of a single fundamental quantity. The total quantum number was considered to be the sum of two other numbers, one giving the units of angular mo-

mentum and the other the units of radial momentum, that is, momentum in the direction of the radius. These numbers fix the size and shape of the orbits. Figure 2 represents these orbits for the total quantum number,  $N = 1, 2, \text{ and } 3$ , and the angular momentum as given by the subscripts. The radius of the  $1_1$  orbit is  $0.529 \times 10^{-8} \text{ cm}$ .

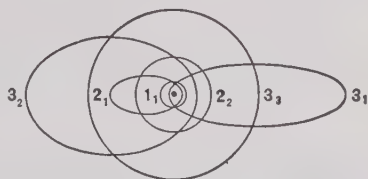


FIG. 2. Electron orbits of hydrogen as pictured by Bohr.

While the existence of discrete energy states rests upon experimental facts, the Bohr theory has had to be modified so that the orbits no longer have their former clear-cut meaning. The changes are due to the discovery that some sort of wave motion is associated with a moving particle. This has led to modifications in the equations of motion to give probabilities rather than precise answers. The orbits are now generally referred to as eigen functions, or **orbitals**, from which the probability of finding the electron in a given region may be determined. Figure 3 is a schematic representation of the wave mechanic picture and may be considered as a composite of the electron in many positions to give an average electron density. The electrons are designated as  $s, p, d, f, g \dots$  corresponding to  $0, 1, 2, 3, 4 \dots$  units of angular momentum.

2. The same general quantum relations as outlined above hold for the other elements, complicated, however, by the facts: (1) that the positive center is no longer a simple unit charge but a complex structure with a net positive charge equal to the atomic number, and (2) that the number of electrons is not one, but a number equal to the atomic number. It is the distribution of these electrons among the various quantum states that determines the grouping of the elements into the so-called "chemical families." The maximum number of electrons in any atom that can have the same total quantum number  $N$  is  $2N^2$ , e.g. for  $N = 1$ , the

maximum number of electrons is 2; for  $N = 2$ , it is 8. Hence when the first quantum level is complete with the second element, helium, the three electrons of the third element, lithium, cannot all remain in the first level, but one of them is forced into the second. With each succeeding element of higher atomic number, the number of electrons in the second level increases until it is filled with eight electrons, i.e. in neon. Each alkali metal marks the beginning of a

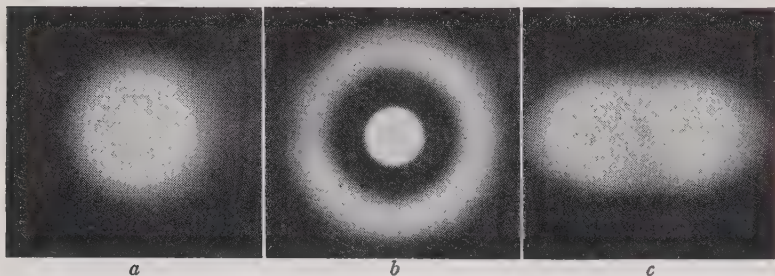


FIG. 3. Different states of the hydrogen atom (after H. E. White): *a*, the atom with a 1 *s* electron; *b*, 2 *s* electron; *c*, one of the states with a 2 *p* electron in a magnetic field.

new quantum group and each noble gas the completion of a group.

Each orbital (Par. 1) contains a maximum of two electrons and the total number of electrons for any one value of the total quantum number,  $N$ , and radial quantum number  $l$  is  $2(2l + 1)$ . Thus for the first shell there are two *s* electrons, for the second two *s* and six *p*, for the third, two *s*, six *p*, and ten *d*, and so on. A complete table of the distribution of the electrons in the various atoms is given in Appendix XVIII. The magnetic properties of the electron indicate that it has a quantized spin motion. However when an orbital contains two electrons, the resultant magnetic spin moment is zero, that is, the two spins are in opposite directions.

**3. Occurrence of Hydrogen.**—Only about one per cent by weight of the earth's crust (outer 10 miles) is hydrogen.

However, if the composition is expressed in terms of the number of atoms, it may be stated that about sixteen per cent of all the atoms on the earth's surface are hydrogen, being second in abundance to oxygen. The major portion of the earth's hydrogen is combined with oxygen in water. It also frequently occurs combined with sulfur, carbon, nitrogen, and chlorine, and less frequently with the other halogens and phosphorus. Hydrogen is a constituent of all acids, and of all animal and vegetable tissue. Only a trace of free hydrogen is found in the atmosphere, about  $1 \times 10^{-3}$  per cent by volume. Larger quantities are sometimes found in volcanic and other natural gases. The spectrum of the sun indicates that enormous flames of incandescent hydrogen are frequently shot out distances of thousands of miles.

**4. Molecular Hydrogen.**—Atomic hydrogen combines to form the molecule  $H_2$ . Representing the proton by **H**, and the electron by a dot, we may write **H:H** as the electronic formula of the molecule, indicating that the two electrons constitute a bond holding the protons together. Due to the spin of the protons, two forms of the molecule exist: para- with spin directions opposed and ortho- with the spins the same. At room temperature the gas is  $\frac{1}{4}$  para- and  $\frac{3}{4}$  ortho- in an equilibrium mixture. Equilibrium at the boiling point gives almost pure para- but the change from the high temperature mixture is slow. It is however catalyzed by charcoal and other surfaces. The boiling point of pure para-hydrogen is  $20.25^\circ \text{K}$ .

Hydrogen has the lowest molecular weight and hence the smallest density of any substance, and, with the exception of helium, the lowest melting point and the lowest boiling point. The gas is odorless, tasteless, and colorless. The most important physical constants are collected in Table I.

Hydrogen was first liquefied by Dewar (1898). The gas in expanding from high pressure to low pressure is

TABLE I

## PHYSICAL CONSTANTS OF HYDROGEN

Melting point, ° C.....	— 259.2	Density g./liter at 0° and	
° A.....	13.9	760 mm.....	0.08985
Heat of fusion, cal. per mole.....	28	Density of liquid g./cc.....	0.071
Boiling point, ° C.....	— 252.7	Solubility in water at 25°	
° A.....	20.4	vol. per 100 vol. of H <sub>2</sub> O. . .	1.8
Heat of vaporization, cal. per mole.....	218	Heat of dissociation, H <sub>2</sub> = 2H cal. per mole.....	103,730
Critical temperature, ° C..	— 241	Per cent H <sub>2</sub> dissociated at 1 atm. total pressure	
° A..	32	At 2,500° A.....	1.3
		3,500° A.....	29.7
Critical pressure, atmos...	20		

heated at ordinary temperatures, but if cooled in liquid air ( $-185^{\circ}\text{C.}$ ), the sign of this heat is reversed. Advantage is taken of this fact in the liquefaction process. (For further discussion of liquefaction process cf. **III—6.**) The metals of the nickel, palladium, platinum groups occlude or dissolve hydrogen to a remarkable degree. Under certain conditions one volume of palladium will take up almost 900 volumes of hydrogen at  $20^{\circ}$  and 1 atmosphere. (Cf. Palladium, **XX—27.**) Molecular hydrogen has a very high relative rate of diffusion since this property is inversely proportional to the square root of the density. Thus the densities of hydrogen and oxygen are in the ratio of 1/16 and hydrogen diffuses four times as fast as oxygen.

**5. Reactions of Hydrogen.**—Hydrogen combines directly with most of the lighter elements, accompanied in the case of the more electronegative elements with the evolution of large amounts of energy; e.g. a jet of hydrogen burns readily in an atmosphere of oxygen or chlorine, and its mixtures with these gases are highly explosive.

The electron formulas of the compounds with the elements from lithium to fluorine are as follows:



Element							
Li ·	Be:	·B:	:C:	:N:	:Ö:	:F:	
Compound							
Li:H	H:Be:H	$\begin{array}{c} \text{H} \\ \text{H}:\ddot{\text{B}}:\text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \text{H}:\ddot{\text{C}}:\text{H} \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \text{H}:\ddot{\text{N}}:\text{H} \end{array}$	$\begin{array}{c} \text{H}:\ddot{\text{O}}:\text{H} \end{array}$	$\begin{array}{c} \text{H}:\ddot{\text{F}}: \end{array}$	

From  $\text{CH}_4$  to  $\text{H}_2\text{O}$  the four pairs of electrons have tetrahedral symmetry. Thus in  $\text{H}_2\text{O}$  the molecule is not linear as indicated in the electron formula given above, but the hydrogens are located approximately at corners of a tetrahedron.

The more negative the element, the more completely does it tend to acquire the electrons of hydrogen, thus leaving the hydrogen with a charge of  $+1$ . The more positive elements, on the other hand, tend to lose their electrons to hydrogen, giving it a charge of  $-1$ , since, as mentioned in Paragraph 2, there is room for two electrons in the first quantum state of the hydrogen atom. In this respect hydrogen resembles the halogen family, all members of which lack one electron of completing the noble gas structure.

Hydrogen in the  $-1$  state is known as hydride. The ion in water solutions is unstable with respect to the reaction



For the hydride potential see Appendix II. The details of the reactions of hydrogen will be discussed under the various elements, although the general reaction of hydrogen to hydrogen ion is to be considered under the following topic.

**6. Properties of the Hydrogen Ion.**—Hydrogen ion is the substance present in all solutions of strong acids and its properties are the familiar properties common to all acids, such as sour taste, characteristic color changes with organic indicators, e.g. the change of blue litmus to red, the neutralization of bases, and the solution of base metals. A

complete statement of the properties of hydrogen ion would include values for the degree of dissociation, volatility, and solubility of all of its compounds, since these quantities determine the extent to which hydrogen ion will unite with negative ions. For example, the statement that the concentrations of hydrogen ion and hydroxide ion in pure water are  $10^{-7}$  moles per liter is equivalent to saying that the reaction,  $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$ , takes place until the concentrations of the ions reach this value. Likewise the statement that the volatility of hydrogen chloride from its water solution is high at  $100^\circ \text{C}$ . is equivalent to saying that the reaction,  $\text{H}^+ + \text{Cl}^- = \text{HCl (gas)}$ , has a strong tendency to take place at this temperature.

7. Many of the most important reactions of hydrogen ion and hydrogen gas may be summarized in terms of the oxidation-reduction couple,  $\frac{1}{2}\text{H}_2 = \text{H}^+ + e^-$ . (The electron will be denoted by a dot in certain structural formulas, as in Paragraph 5, but in writing ordinary equations, we will use the symbol  $e^-$ .) For example, zinc will displace or liberate hydrogen from acids because the reaction,  $\text{Zn} = \text{Zn}^{++} + 2e^-$ , gives a higher "pressure" (voltage) of electrons. The total reaction,  $\text{Zn} + 2\text{H}^+ = \text{Zn}^{++} + \text{H}_2$ , is the result of the transfer of the electrons from the zinc to the hydrogen ion. On the other hand, the reaction  $\text{Ag} = \text{Ag}^+ + e^-$  has a lower voltage than hydrogen; and hydrogen reduces silver ion,  $2\text{Ag}^+ + \text{H}_2 = 2\text{Ag} + 2\text{H}^+$ , by the transfer of electrons from the hydrogen to the silver ion. Reference may be made to the table of oxidation-reduction potentials (Append. II) for the position of hydrogen in respect to a large number of oxidation-reduction couples. Mention should be made of the fact that the oxidation of metals by hydrogen ion is often a slow reaction, and that the speed depends greatly upon the nature of the surface upon which the gas deposits. Thus the action of acid upon zinc proceeds very slowly if the zinc is pure, and rapidly only when impurities are present. The power of

hydrogen ion as an oxidizing agent depends, of course, upon its concentration. In normal alkaline solution, a stronger reducing agent is required to liberate hydrogen than in acid since the potential of the reaction,  $\frac{1}{2}\text{H}_2 + \text{OH}^- = \text{H}_2\text{O} + e^-$ , is 0.83 volt more positive than the potential of the acid couple.

Although the formula of hydrogen ion in water solution is written as  $\text{H}^+$ , the ion exerts such a strong attraction upon the water molecules that it might be written  $\text{H}(\text{H}_2\text{O})_n^+$ . The energy of hydration of the hydrogen ion, approximately 250,000 cal., is larger than that of any other singly charged ion.

**8. Preparation.**—Although hydrogen is liberated by the action of the electropositive metals, such as sodium, potassium, and calcium upon water, these metals are too expensive for its practical preparation. Hydrogen is sometimes prepared by passing steam over finely divided iron heated to redness.  $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$ . The gas is conveniently prepared in the laboratory by the action of dilute sulfuric or hydrochloric acid upon zinc or aluminum. Hydrogen so prepared usually contains small quantities of volatile hydrogen compounds resulting from the presence of impurities in the metals. These may be removed by bubbling the gas through a permanganate solution. Water vapor is conveniently removed by contact with concentrated sulfuric acid.

There are four principal sources of commercial hydrogen: the reduction of water by carbon, the destructive distillation of coal, the cracking of methane,  $\text{CH}_4$ , and the electrolysis of aqueous solutions. The reduction of water by carbon involves the water gas reaction:  $\text{H}_2\text{O} + \text{C} = \text{CO} + \text{H}_2$ , and the further reaction,  $\text{H}_2\text{O} + \text{CO} = \text{H}_2 + \text{CO}_2$  (cf. XIII—6). Coke-oven hydrogen is a by-product of the destructive distillation of coal and contains large quantities of methane, which may be removed by liquefaction. Electrolytic hydrogen is now usually prepared by the electrolysis

of concentrated sodium hydroxide solutions with iron or nickel electrodes. Hydrogen is liberated at the cathode and oxygen at the anode. The gas is quite pure except for a small quantity of oxygen which is present by diffusion from the anode. This may be removed by passing the gas over a catalyst, e.g. finely divided nickel at  $250^{\circ}\text{C.}$ , which accelerates the combinations of hydrogen and oxygen. Large quantities of hydrogen are also formed as a by-product in the manufacture of sodium hydroxide (cf. **IV—12**) by the electrolysis of salt brine.

**9. Commercial Uses.**—The oxy-hydrogen flame is used in cutting and welding metals. The temperature of the flame is approximately  $2,500^{\circ}\text{C.}$  A special burner is employed which prevents the explosion of the gases by mixing them just before they reach the orifice. The atomic hydrogen torch, recently developed, has many advantages in welding under reducing conditions. The atomic hydrogen is formed by blowing hydrogen through a very hot electric arc. The metal surface acts as a catalyst for the union of the atomic hydrogen and is heated to a high temperature, estimated between  $4,000$  and  $5,000^{\circ}\text{C.}$ , by the heat liberated through the formation of the  $\text{H}_2$  molecule.

Large quantities of hydrogen are consumed in the manufacture of synthetic ammonia by the direct union of the elements. The synthetic production of methanol,  $\text{CH}_3\text{OH}$ , and other liquid fuels by the reaction of hydrogen and carbon monoxide in the presence of catalysts promises to become of great industrial significance. Another important use is in the hydrogenation of many oils, such as cotton-seed oil, to form solid fats.

Hydrogen is also employed as a lifting medium in balloons. Its efficiency depends upon the difference in weight of equal volumes of hydrogen and air. This is 1.2 grams per liter at  $0^{\circ}\text{C.}$  and 1 atmosphere.

**10. Analytical.**—Hydrogen is often determined by mixing with an excess of oxygen and passing the mixture over a

glowing filament electrically heated. The per cent of hydrogen is calculated by the contraction in volume due to the formation of water. Hydrogen is also determined by passing the gas over hot copper oxide,  $\text{CuO} + \text{H}_2 = \text{Cu} + \text{H}_2\text{O}$ , and absorbing the water in a weighed tube of calcium chloride.

**11. Deuterium.**—Since the mass of deuterium is approximately double that of ordinary hydrogen, its **nucleus** may be considered to be composed of one proton and one **neutron**. The resulting charge is one positive so the atom has but one “orbital” electron. The electron energy levels are almost identical with those of the mass one isotope and the principal differences in the physical and chemical properties of the two isotopes are due to the difference in the energy of vibration of the two atoms in their various molecules. For example, the energy of dissociation of  $\text{D}_2$  is 1.8 kcal. larger than that of  $\text{H}_2$  because of the difference in energy of the vibrational states. Similar differences in the energies of the bonds of hydrogen and deuterium to oxygen exist in the oxides  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . The heat of vaporization of  $\text{D}_2\text{O}$  is about 260 cal. per mole greater than that of  $\text{H}_2\text{O}$ .

TABLE II

## PHYSICAL CONSTANTS OF DEUTERIUM AND HEAVY WATER

Atomic weight D.....	2.00147	Density $\text{D}_2\text{O}$ 25° C. ....	1.1066
Boiling point $\text{D}_2$ , ° A.....	23.5	Melting point $\text{D}_2\text{O}$ ° C... ..	3.82
Freezing point $\text{D}_2$ , ° A.....	18.7	Boiling point $\text{D}_2\text{O}$ ° C... ..	101.42
$\text{D}_2 = 2\text{D}^+$ (in pure $\text{D}_2\text{O}$ )		Temperature of maximum	
+ $2e^-$ E° (volts).....	0.0046	density, ° C.....	11.6
		$\text{D}_2\text{O} = \text{OD}^- + \text{D}^+$ $K_{25^\circ}$ .	$0.3 \times 10^{-14}$

The preparation of pure deuterium was first carried out by the fractional electrolysis of a sodium hydroxide solution with nickel electrodes; the hydrogen evolved at the cathode is 5 to 8 times poorer in deuterium than the water and the heavier isotope thus accumulates in the residues.

Concentration of DHO and  $D_2O$  in water may also be effected in an efficient distilling column.

The replacement of hydrogen atoms by deuterium in organic molecules has opened many new fields of investigation into the mechanism of organic and biochemical reactions.



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## Chapter II

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### INERT GASES: HELIUM, NEON, ARGON, KRYPTON, XENON, RADON

1. As early as 1784, Cavendish showed that air contained a small amount of an unknown gas which was quite non-reactive, but further work on the subject was not published until 1893, when Lord Rayleigh found that the weight of 1 liter of nitrogen prepared from pure nitrogen compounds was 1.2506 g., as compared to 1.2572 g. for atmospheric nitrogen. This discrepancy led to a careful investigation of atmospheric nitrogen by Rayleigh and Ramsey and to the discovery of argon. Ramsey shortly after identified the gas given off by uranium minerals as the unknown element, helium, whose existence Lockyer had postulated in 1868 to account for a prominent yellow line in the solar spectrum. Subsequent investigation by fractional distillation of the crude argon obtained from air led to the discovery of neon, krypton, and xenon, the percentage of the various gases in air being:

He	Ne	A	Kr	Xe
0.0004	0.0012	0.94	0.00005	0.000006 per cent

The natural gas fields of Texas and Kansas contain helium in small amounts, a number of these wells, high in nitrogen content, analyzing between 1 and 2 per cent of the gas.

Research on the radioactive elements (Chap. XXI) has

shown that the so-called alpha-ray, or particle, is doubly charged helium, and that helium is thus one of the products of the decomposition of these unstable elements. It has been calculated that a gram of radium produces 0.11 cc. of helium per year, and a gram of uranium oxide,  $\text{U}_3\text{O}_8$ ,  $9.1 \times 10^{-8}$  cc. The radioactive mineral monazite contains about 1 cc. of helium per gram. The loss of an alpha particle by radium or its isotopes results in the formation of the heaviest member of the inert gas group, radon, also called niton. Radon, however, is very unstable, the average life of an atom being only a few days (Chap. XXI).

**2. Physical Properties.**—The more important physical properties have been summarized in Table I. The gases are all monatomic, and the low values of the boiling points indicate that their atoms have very little attraction for each other. Indeed, the helium atom is so inert that this element possesses the lowest boiling point of any substance, and by

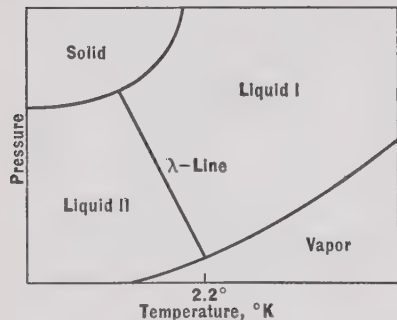


FIG. 1. Diagrammatic representation of the phases in helium at low temperatures.

boiling under reduced pressure (below 0.01 mm.), a temperature of  $0.7^\circ$  absolute has been obtained. Considerable pressure (140 atm. at  $4.2^\circ$ ) is required to cause liquid helium to solidify and the force of attraction is so small that the heat of solidification at the lowest temperatures is practically zero. Like hydrogen, helium gas heats slightly

when expanded at ordinary temperature and the gas must be cooled to the temperature of solid hydrogen (about  $11^\circ \text{A.}$ ) before it can be cooled by free expansion.

When liquid helium is cooled to  $2.2^\circ \text{A.}$  a remarkable transition occurs, for example, the viscosity decreases and the thermal conductivity increases. The substance seems

TABLE I  
ATOMIC AND PHYSICAL PROPERTIES

	He	Ne	A	Kr	Xe	Rn
Atomic number.....	2	10	18	36	54	86
Atomic weight.....	4.00	20.2	39.91	82.9	130.2	222
Stable isotopes.....	3, 4	20, 21, 22	36, 40	84, 86, 82, 83, 80, 78	129, 132, 131, 134, 136, 128, 130, 126, 124	(222) (220)
Electrons in various quantum levels,						
1st.....	2	2	2	2	2	2
2d.....		8	8	8	8	8
3d.....			8	18	18	18
4th.....				8	18	32
5th.....					8	18
6th.....						8
Melting point, ° C.....	- 268.9 (140 atm.)	- 248.5	- 189.3	- 156.6	- 111.5	- 71
° A.....						
Boiling point ° C.....	4.2	24.6	83.8	116.5	161.6	202
° A.....	- 268.9	- 245.9	- 185.8	- 152.9	- 108.0	- 61.8
Heat of vaporization, cal. per mole, at	4.22	27.2	87.3	120.2	165.1	211.3
B.P.....	25	405	1,600	2,240	3,100	3,600
Critical temperature, ° C.....	- 268	- 220	- 117	- 63	15	
Density of liquid.....	0.126	1.20	1.40	2.6	3.06	4.4
Potential required to ionize gas atoms, volts,						
1st electron.....	24.46	21.45	15.68	13.93	12.08	10.70
2d electron.....	54.14	40.9	27.76	ca 26	ca 21	—

to be a solid with properties of a gas. This appears to be a different state of matter and it is referred to as a degenerate gas. The phase relations are indicated in Fig. 1.

The inert gases are somewhat soluble in water and the solubility increases markedly with increasing atomic weight. Helium and neon are not appreciably absorbed by charcoal cooled in liquid air, but the heavier gases are readily absorbed.

The potentials required to remove electrons from the gaseous atoms are relatively high (Table I) but ionization is, of course, produced when the gas is subjected to an electrical discharge, i.e. bombarded with high speed electrons. The gas under the influence of such a discharge is luminous, due to the light emitted upon the recombination of the electron with the atom, and the characteristic spectrum of each of the elements, thus produced, serves as a ready means of identification.

**3. Electron Structure and Chemical Properties.**—The configuration of the electrons in the various atoms of the group is important, not only as explaining their inertness, but also in connection with the interpretation of the formation of the great majority of chemical compounds. Each inert gas marks the completion of an outer shell of eight electrons, except in the case of helium which completes the first quantum group containing but two electrons (Table I). These completed groups are so stable that not only are the ionization potentials of the inert gases very high, but the elements preceding and following each inert gas readily gain or lose sufficient electrons to form ions with the same electronic structure, i.e. the completed octet. This is illustrated by the following ions all with the electron structure of neon:

	O <sup>2-</sup>	F <sup>-</sup>	Ne	Na <sup>+</sup>	Mg <sup>2+</sup>
Nucleus . . . . .	+ 8	+ 9	+ 10	+ 11	+ 12
Electrons in 1st group . . . . .	2	2	2	2	2
2d group . . . . .	8	8	8	8	8

Thus the formation of many binary compounds consists in the transfer of electrons from a metallic element to a non-metallic element with the formation of positive and negative ions of the inert gas type, e.g. in the ions shown above:  $\text{Na} + \text{F} = (\text{Na}^+)(\text{F}^-)$ , and crystals of such compounds are lattices built up of these ions (cf. Append. V for many lattice types). However, it is not to be inferred that all positive ions are of the inert gas type, as most of the noble metals form ions of somewhat different structure (cf. VII—1).

Although the statement is generally made that the inert gases form no compounds, a few relatively unstable compounds do exist. Thus helium and hydrogen gases subjected to an electrical discharge contain small amounts of the ions,  $\text{HeH}^+$  and  $\text{HeH}_2^+$ , and the large solubility of the heavier members of the group indicates the formation of unstable hydrates. It is claimed that under a pressure of 15 atmospheres at  $0^\circ$ , krypton forms the hydrate,  $\text{Kr} \cdot 5\text{H}_2\text{O}$ . A series of compounds, stable below  $-130^\circ$ , has been reported for argon and boron trifluoride, e.g.  $\text{A}(\text{BF}_3)$ ,  $\text{A}(\text{BF}_3)_2$ ,  $\text{A}(\text{BF}_3)_6$ .

**4. Commercial Preparation and Uses.**—The United States government operates a plant in Texas for the extraction of helium from natural gas. During the period 1929 to 1937 approximately eighty million cubic feet of the gas were extracted. The process is one of fractional liquefaction. The gas is used in dirigibles and balloons as it has a lifting power only about 10 per cent less than hydrogen and is, of course, non-combustible.

Helium has assumed considerable importance in deep diving and in deep caisson operations, where men engaged are subject to "caisson disease." This is due to the solution of nitrogen in the blood at high pressure, and its subsequent escape when the pressure is lowered, forming bubbles in the capillaries, or in the brain or spinal cord. It has been shown that the time required in coming out from under high

pressure is greatly reduced by the substitution of a mixture of oxygen and helium for compressed air, on account of the small solubility of helium. Mixtures of helium and oxygen are also used in treatment of acute cases of asthma and other diseases where there is constriction of the air passages.

The very low boiling point of helium makes it of special importance in the investigation of the behavior of substances in the neighborhood of absolute zero. Among the more significant changes at these temperatures is the disappearance of the specific heat and coefficient of expansion of solids, and the electrical resistance of many metals. Although, in general, the resistance of metals decreases with decreasing temperature, there is often an abrupt drop a few degrees above absolute zero: thus, at  $7^{\circ}$  A., the resistance of lead suddenly decreases a million-fold.

The neon tubes used in electric signs contain the gas under low pressure. The commercial source of the element is the fractionation of atmospheric argon.

Argon is now used extensively in filling electric light globes. The presence of the inert gas decreases the rate of evaporation of the filament, retards the blackening of the bulb, and makes possible the operation of the lamp at a higher temperature, thus greatly increasing its efficiency.



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# Chapter III

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## OXYGEN

1. The elements of Group VI,—oxygen, O, sulfur, S, selenium, Se, and tellurium, Te, are characterized by the presence of six outer or valence electrons, and the tendency to complete the octet of the noble gas structure by the addition of two electrons. Consequently these elements readily form compounds in which they have an **oxidation state** of  $-2$ . This tendency is the greatest with the smallest atom; hence oxygen is the strongest oxidizing agent and tellurium the weakest. On the other hand the six valence electrons of the neutral atom may be removed, wholly or in part, giving positive oxidation states up to six. In the case of oxygen this can only be done by high potentials in the gas at low pressure, as no other element is capable of removing electrons from oxygen; hence no ordinary compounds exist in which the oxygen atom must be considered as having a positive charge (with possible exception of  $F_2O$ ). This separates it considerably in chemical behavior from the other members of the group, and suggests its separate consideration.

2. **Occurrence.**—Approximately half by weight of the material of the earth's crust is oxygen, and since the atomic weight of oxygen is less than the average atomic weights of the other elements, it follows that more than half of all the atoms of the earth's crust are oxygen. The most abundant of its compounds are those with silicon and aluminum. The element occurs in the free state in the atmosphere,

which is one fifth oxygen by volume. Eight ninths by weight of water and between 40 and 50 per cent of all rocks is oxygen. Compounds are known with all the elements except the noble gases.

**3. Physical Properties.**—In common with the other elements of the family, oxygen exists in several molecular forms. In the gaseous state there are two modifications, ordinary oxygen,  $O_2$ , and ozone,  $O_3$ . These and probably  $O_4$  also can exist as liquids. Solid oxygen exists in at least three modifications. The more important properties of the oxygen atom and the  $O_2$  molecule are given in Table I.

TABLE I  
ATOMIC AND PHYSICAL PROPERTIES OF OXYGEN

Atomic number.....	8	Density g. per cc. 0° C. and 1 At.,.....	
Nucleus { neutrons.....	8	gas.....	0.0014290
{ protons (+).....	8	liquid - 183°.....	1.13
Atomic weight.....	16.00	Vaporization at 1 At. Temperature ° A. ....	90.1
Isotopes.....	16	Heat, cal.....	1629
traces of 17 and 18		Fusion Temperature ° A. ....	54.4
Electrons in various energy levels, 1st.....	2	Heat, cal.....	105
2d.....	6	Transition Solid <sub>1</sub> = Solid <sub>2</sub> Temperature ° A.....	43.7
Ionization potential, volts		Heat, cal.....	177
1st electron.....	13.55	Transition Solid <sub>2</sub> = Solid <sub>3</sub> Temperature ° A. ....	23.7
2nd electron.....	34.93	Heat, cal.....	17.5
Electron affinity, volts		Solubility per 100 g. water 0° C.....	0.007
1st electron.....	2.2	25° C.....	0.004
2nd electron.....	- 9.5	100° C.....	0.001
Heat of dissociation of $O_2$ molecule, kcal.....	117.3		
Dielectric constant of liquid.	1.47		
Magnetic moment of liquid $O_2$ compared to iron as unity.....	0.001		
Size of $O^-$ in crystals, cm. $\times 10^8$ .....	1.40		

The oxygen molecule  $O_2$  is highly magnetic, and since this property is associated with atoms having an odd number of electrons, it is assumed that the electron formula for the molecule is  $\ddot{O}:\ddot{O}$ : rather than  $:\ddot{O}::\ddot{O}:$  or  $:\ddot{O}:\ddot{O}:$ .

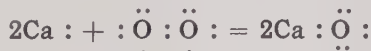
The variation with concentration of certain of the properties of liquid oxygen dissolved in liquid nitrogen may be explained on the assumption of an equilibrium,  $2\text{O}_2 = \text{O}_4$ . The change of this equilibrium with temperature may explain the very large coefficient of expansion of the liquid. In harmony with the assumed structure of  $\text{O}_2$  the most likely structure of  $\text{O}_4$  would be



However the small energy of formation of  $\text{O}_4$  suggests that the bonds between the two  $\text{O}_2$  molecules are not true electron pair bonds.

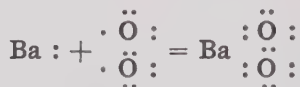
**4. Chemical Properties.**—Oxygen combines directly with all other elements except the halogens, the noble gases, and a few of the most noble metals, and in many of these reactions sufficient energy is evolved to heat the products to the point of incandescence, as in the familiar burning of carbon in air. Very often reactions of oxygen which are rapid at high temperatures will not proceed at low temperatures; thus carbon must be heated before it ignites in air, but many oxidations do go slowly in the cold, e.g. the rusting of iron.

A compound of oxygen with another element is called an oxide, and the oxidation state of  $-2$  (except in peroxides, Par. 11) is assigned to the oxygen indicating that it has gained two electrons, e.g.

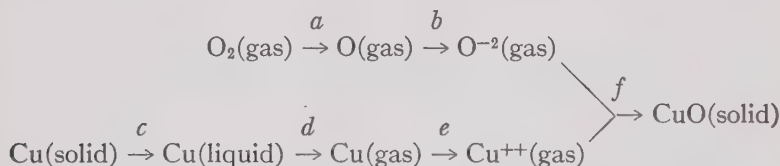


**5.** The slowness of many oxygen reactions is doubtless connected with the large energy required to dissociate the oxygen molecule into atoms. Indeed the probable mechanism of most reactions of oxygen is first the addition of two electrons to the  $\text{O}_2$  to form a peroxide, where the bond be-

tween the oxygen atoms remains unbroken, as illustrated by:



The process of oxidation may be examined in detail by arbitrarily dividing the formation of an oxide into the following steps. (This does not imply that the process of oxidation ordinarily occurs in this way.) Using copper oxide by way of illustration:



The dissociation of the oxygen molecule, step *a*, involves the absorption of a large amount of energy, as do also steps *c* and *d*, which represents the detachment of copper atoms from the solid mass. The removal of electrons from the metal, step *e*, requires the absorption of still more energy (i.e. the ionization potential). The addition of two electrons to the oxygen atom, step *b*, also requires energy; although it is not large, because of the tendency to complete the octet. It is step *f* which is chiefly responsible for making the net result of the whole process an evolution of energy, and this step must be very large in order to overcome the energy absorption of steps *a*, *b*, *c*, *d*, and *e*. Now it is very illuminating to note that step *f* depends for positive ions of the same charge chiefly upon the size of the ions, being greater the smaller the positive ion. Furthermore, the great stability of oxides, as compared with many other binary compounds, depends upon the fact that the oxygen ion is one of the smallest negative ions. The effect of step *f*, for example, makes the heat of formation of lithium oxide, 142 kcal., greater than that of sodium oxide,

101 kcal., in spite of the fact that more energy is absorbed in removing the electron from lithium than from sodium.

The above scheme throws light upon differences in the heat of combustion of other substances. Thus a metal of high melting and boiling point, such as platinum, owes its noble character in part to high values for steps *c* and *d*, and not entirely to a high value for step *e*. Again, the high stability of silicon dioxide is related to the large energy evolution of step *f*, which may be inferred from its high melting point and great hardness.

**6. Preparation and Uses.**—Commercial oxygen is now prepared on a large scale by the fractional distillation of liquid air. The principle of the method may be understood by considering the liquid vapor diagram, Fig. 1, for solutions of oxygen and nitrogen. Nitrogen boils at  $-195^{\circ}\text{C}$ . and oxygen at  $-183^{\circ}\text{C}$ . At intermediate temperatures, a solution of the two liquids in equilibrium with the vapors has the composition *b* and the vapor, the composition *a*. Since the gas phase is much richer in nitrogen than the liquid, evaporation results in the liquid becoming richer in oxygen. Simply boiling off the nitrogen from liquid air would not give an efficient separation of the two gases, so the process is carried out in a fractionating column. The cold liquid enters the top of the column; as the liquid evaporates the temperature rises and the liquid increases in oxygen content; the vaporized gas passes up through the colder liquid and loses oxygen, becoming almost pure nitrogen. Oxygen cannot be liquefied above its critical temperature,  $-118^{\circ}\text{C}$ ., by any pressure, however great; but the fact

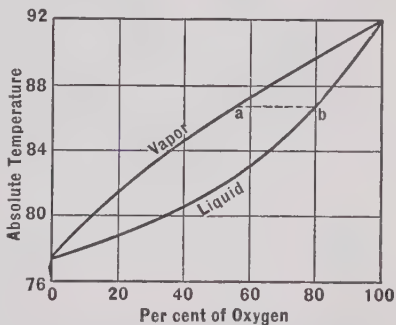


FIG. 1. Temperature-composition diagram for liquid oxygen and nitrogen.

that compressed air at room temperature cools upon expanding, due to the work done in overcoming the attraction between the molecules (Joule-Thomson effect), makes possible the Linde liquefaction process. Air is compressed to about 3,000 lb. per sq. in. and allowed to expand. The cool expanded air is led back over the incoming highly compressed air and cools it until finally the temperature drops sufficiently below the critical temperature to permit liquefaction. In the Claude process the compressed air is subjected to an additional cooling effect by doing external work. Some commercial oxygen is prepared by the electrolysis of water; however, unless the electrical energy is very cheap and there exists a ready market for the hydrogen produced at the same time, the electrolytic process cannot compete with the liquid air process.

Barium peroxide was formerly an important source of oxygen, since the reaction,  $\text{BaO} + \frac{1}{2}\text{O}_2 = \text{BaO}_2$ , is easily reversible. The process was usually carried out at  $700^\circ \text{C}.$ ; the barium peroxide being first formed from air at a pressure of about 3 atmospheres, and the oxygen then pumped off by reducing the pressure.

Sodium peroxide (cf. IV-11) is a convenient source of oxygen in small quantities. A common laboratory method for the preparation of oxygen consists of the decomposition of potassium chlorate using manganese dioxide as a catalyst at about  $200^\circ \text{C}.$ :  $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$ . In the absence of a catalyst, oxygen is evolved but slowly; most of the chlorate being converted into perchlorate, which is much more stable. In the early investigations of oxygen by Scheele, Priestley, and Lavoisier (about 1775) much use was made of the compounds  $\text{HgO}$ ,  $\text{MnO}_2$ ,  $\text{PbO}_2$ , and  $\text{KNO}_3$ , all of which give oxygen upon heating.

The present commercial importance of oxygen has resulted from the development of the oxy-acetylene torch in welding and cutting metals. Oxygen for this purpose is sold in heavy cylinders under a pressure of about 2,000 lb.

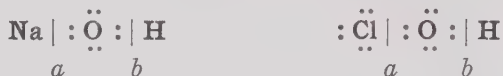


per sq. inch. The oxy-hydrogen torch, although not producing as high a temperature as the oxy-acetylene flame, is also of wide industrial use. Pure oxygen is used in the treatment of pneumonia and in cases of asphyxiation; and mixtures of oxygen with nitrous oxide or ether are administered in producing anesthesia. It is also used to maintain the oxygen content of the air in submarines. The "hardening" of certain oils is accelerated by using pure oxygen. Charcoal, cotton, or other cellulose soaked in liquid oxygen form high explosives known as "oxylignite."

**7. Oxides, Bases, Acids.**—The various types of oxides with different elements correspond to all the possible oxidation states of the positive elements from + 1, as in  $\text{Cu}_2\text{O}$ , to + 8, as in  $\text{OsO}_4$ . In addition, a number of mixed oxides occur with elements forming oxides of more than one state, for example  $\text{Pb}_3\text{O}_4$ , which is  $(\text{PbO})_2\text{PbO}_2$ , and  $\text{Fe}_3\text{O}_4$ , which is  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ . In the crystalline state, if the force of attraction between the positive kernel and the oxide ion is not too great, the oxides crystallize in the completely polar type of structure: for example, the  $\text{CaO}$  crystal is a lattice of  $\text{Ca}^{++}$  and  $\text{O}^{--}$  similar to the sodium chloride structure, and there are no molecules of  $\text{CaO}$ . On the other hand, large attractive forces allow the molecule to preserve its identity in the solid as in carbon dioxide.

Oxides of metal ions with small positive charge react with water to form bases, e.g.  $\text{Na}_2\text{O} + \text{H}_2\text{O} = 2\text{NaOH}$ ,  $\text{MgO} + \text{H}_2\text{O} = \text{Mg}(\text{OH})_2$ ; while oxides of non-metals, and even of metals in the higher oxidation states react with water to form acids: e.g.  $\text{Cl}_2\text{O} + \text{H}_2\text{O} = 2\text{HOCl}$ ;  $\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_3$ ;  $\text{CrO}_3 + \text{H}_2\text{O} = \text{H}_2\text{CrO}_4$ ;  $\text{As}_2\text{O}_5 + 3\text{H}_2\text{O} = 2\text{H}_3\text{AsO}_4$ . In all of these compounds an atom of oxygen separates a hydrogen atom from the remainder of the molecule; and the basic or acidic character seems to depend largely upon the relative attractive forces between the oxide ion and the hydrogen ion, on the one hand, and the remainder of the molecule on the other, modified by the

energy of hydration of the resulting ions. Thus NaOH is a base because the cleavage occurs more easily at *a*, while HOCl is an acid because it occurs at *b*.



The bond between the sodium and oxygen is largely that of the coulombic attraction [ $E = ee'/(r + r')$ ], while the bond between the chlorine and oxygen has considerable covalent (electron pair) character. The greater ability of the chlorine to take electrons away from the oxygen makes the latter more positive in HClO than in NaOH and, in general, the more positive the oxygen the weaker will be its bond with the hydrogen.

A larger positive charge on an atom also accounts for its greater tendency to give acidic properties. For example, if we compare HClO with HClO<sub>4</sub>,



and consider that in the latter the electrons largely belong to the oxygen, making the chlorine + 7, while in the former the chlorine has lost but 1 electron, making it + 1, we may expect the energy of separation of OH<sup>-</sup> to be roughly seven times as great in the latter. It is, therefore, correspondingly easier for H<sup>+</sup> to be detached from the latter.

Table II illustrates the change from basic to acidic character dependent upon the sizes of the atoms and their charges. We see that similar energy values yield similar characteristics. This treatment is, of course, only approximate. Actually the energies are considerably different than calculated from purely coulombic forces due to the formation of electron pair bonds. However, this coulombic picture is very useful. It cannot be applied to the transition

TABLE II

VALUES FOR  $\frac{e'e}{r+r'}$  FOR OXIDE ION ( $r = 1.40 \cdot 10^{-8}$  CM.)  
AND CERTAIN POSITIVE IONS

	Li <sup>+</sup>	Be <sup>+2</sup>	B <sup>+3</sup>	C <sup>+4</sup>	N <sup>+5</sup>		
Radius cm. $\times 10^8$	0.60	0.31	0.20	0.15	0.11		
$\frac{e'e}{r+r'}$	1.0	2.32	3.74	5.16	6.62		
Hydroxide	LiOH strong base	Be(OH) <sub>2</sub> ampho- teric	B(OH) <sub>3</sub> ampho- teric	CO(OH) <sub>2</sub> weak acid	NO <sub>2</sub> OH strong acid		
	Na <sup>+</sup>	Mg <sup>+2</sup>	Al <sup>+3</sup>	Si <sup>+4</sup>	P <sup>+5</sup>	S <sup>+6</sup>	Cl <sup>+7</sup>
Radius cm. $\times 10^8$	0.95	0.65	0.50	0.41	0.34	0.29	0.26
$\frac{e'e}{r+r'}$	0.86	1.96	3.16	4.42	5.76	7.10	8.44
Hydroxide	NaOH strong base	Mg(OH) <sub>2</sub> weak base	Al(OH) <sub>3</sub> ampho- teric	SiO(OH) <sub>2</sub> weak acid	PO <sub>2</sub> OH strong acid	SO <sub>2</sub> (OH) <sub>2</sub> strong acid	ClO <sub>3</sub> OH strong acid

elements, because of the high bond energies. Thus Pt(OH)<sub>2</sub> is less basic than Ni(OH)<sub>2</sub>.

**8. Analytical Properties.**—Both oxygen and nitrous oxide will cause a glowing splinter to burst into flame, but oxygen may be distinguished from the latter by the production of dark brown fumes with nitric oxide. The gas is usually determined quantitatively in a mixture of gases by determining the decrease in volume upon contact with various liquids or solids which absorb oxygen, such as, (1) a solution of cuprous chloride in hydrochloric acid, (2) alkaline solution of pyrogallol, (3) phosphorus. A very delicate test for small quantities of oxygen is the deep red color produced by the action of oxygen upon an alkaline solution containing ferrous iron and pyrocatechol.

**9. Water.**—Water plays such an important role in chemistry that its physical constants are of especial significance. For a substance of low molecular weight, its **melting point**, 0° C., and **boiling point**, 100° C., are extremely high, indicating high attractive forces between the molecules. The high **dielectric** constant, 81 at 18° C., shows that the molecules are highly polar, which would account for the large intermolecular attraction, since two dipoles would attract

each other. The unusual solvent action of water for salts is also to be correlated with its high dielectric constant, since the force of attraction between ions varies inversely

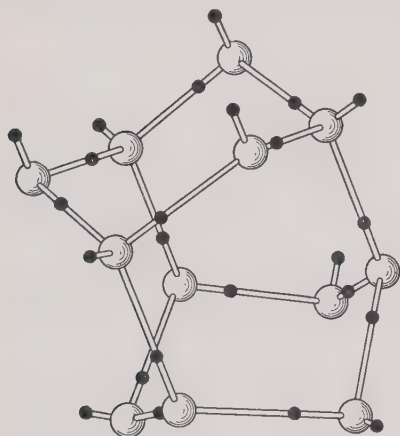


FIG. 2. Arrangement of water molecules in ice.

as the dielectric constant of the medium. Water is unusual in possessing a point,  $4^{\circ}\text{C.}$ , of maximum density (Append. VIII). This may be connected with the fact that water is one of the few substances whose liquid form ( $d = 1.00$  at  $4^{\circ}\text{C.}$ ) is denser than the solid ( $d = 0.917$ ). In ice the molecules are combined in a way that involves a looser packing than in the liquid (cf. Fig. 2), and as the tem-

perature of the liquid approaches  $0^{\circ}$ , there are doubtless formed an increasing proportion of these same molecules in the liquid. This change counteracts the increase in density uniformly found when only one molecular species is present. Complete vapor pressure tables for water and ice are given in Appendix X. The simple phase diagram for "solid, liquid, vapor" is represented in Fig. 3. Since the density of the solid is less than that of the liquid, the melting point is decreased by pressure. At high pressures ice exists in a number of allotropic modifications, and as several of these are denser than the

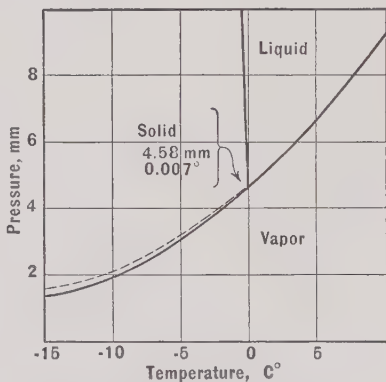


FIG. 3. Temperature-pressure diagram for ice, water, and vapor.

liquid, they may be obtained under high pressure at temperatures above  $0^{\circ}$ , as shown in Fig. 4.

The water molecule may be considered as a tetrahedral oxygen with hydrogens attached to two corners. However the angle is only  $105^{\circ}$  in the gas instead of the tetrahedral angle,  $109^{\circ} 28'$ . Crystal structure data indicate that in the ordinary form of ice each oxygen atom is surrounded by four other oxygen atoms with a hydrogen atom located on the line joining the oxygens, thus forming a hydrogen bond between the oxygens.

The **heat of fusion** is 80 cal. per gram and the **heat of vaporization**, 540 cal. per gram. The **lowering of the freezing point** and the **elevation of boiling point** per mole

of solute in 1,000 g. of water are  $1.86^{\circ}$  and  $0.52^{\circ}$  respectively. The lowering of the freezing point of water by common salt is important in refrigeration. The freezing point diagram is given in Fig. 3, Chapter IV. One of the lowest eutectics given with water is that of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . A mixture of 7 parts of snow and 10 parts of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  gives a temperature of  $-55^{\circ} \text{C}$ . (cf.

Fig. 2, Chap. V). The **surface tension** of water at  $20^{\circ}$  is 72.5 dynes per cm. The **compressibility** at  $20^{\circ}$  is

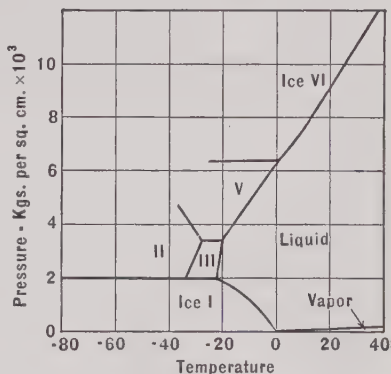


FIG. 4. Modifications of ice at high pressures.

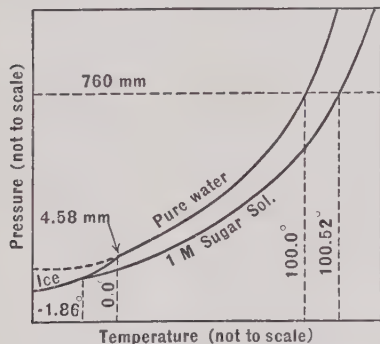


FIG. 5. Diagrammatic representation of the effect of a solute upon the vapor pressure, boiling point, and melting point of water.

$43 \times 10^{-6}$  cc. per megabar. The **specific heat** of 1 g. of water at  $15^\circ$  is taken as unity in the definition of the calorie. The variation of its specific heat with temperature is as follows:  $0^\circ$ , 1.0088;  $30^\circ$ , 0.9988;  $50^\circ$ , 0.9996;  $100^\circ$ , 1.0099. The **heat of formation** per mole of  $\text{H}_2\text{O}$  at  $25^\circ$  is  $-68,270$  cal. The **heat of ionization**,  $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$ ,  $-13,200$  cal. is of course the negative of the heat of neutralization of dilute solutions of strong acids and bases. The constant for a first **ionization** of water is  $1.008 \times 10^{-14}$  at  $25^\circ \text{C}$ . and the constant for the second ionization probably less than  $10^{-36}$ . The **decomposition voltage** of water upon electrolysis is 1.23 volts plus an overvoltage depending upon the nature of the electrodes due to the slowness of the electrode reactions (cf. Append. I). The **specific conductivity** of the purest water at  $20^\circ \text{C}$ . is about  $1 \times 10^{-7}$  reciprocal ohms.

**10.** Water is easily purified from non-volatile substances by distillation; however, to prepare water free from volatile acids, bases, and organic material, elaborate precautions must be taken. This is usually done by first distilling from an alkaline solution of permanganate to remove organic material and volatile acids, especially carbonic, and then redistilling from non-volatile acid solution to remove volatile alkalis, especially ammonium. If the vapor is condensed in air it will contain dissolved gases, hence the distillation is carried out in vacuum. Due to the solubility of glass in water, the condenser is made of quartz, tin, or silver. The so-called "softening of hard water" is discussed under calcium (cf. V—11).

**11. Hydrogen Peroxide.**—The formation of peroxides as intermediate products in the direct oxidation by oxygen has been mentioned (Par. 4). These compounds may be considered as derivatives of hydrogen peroxide,  $\text{H}_2\text{O}_2$ . The oxidation state of the oxygen is  $-1$ . In terms of molecular structure peroxides consist of oxygen linked to oxygen to form the group  $\ddot{\text{O}}:\ddot{\text{O}}:$ .



The oxidation of certain metals by moist oxygen results in the formation of the oxide and hydrogen peroxide: e.g.  $\text{Zn} + \text{O}_2 + \text{H}_2\text{O} = \text{ZnO} + \text{H}_2\text{O}_2$ . The mechanism of this reaction may be the formation of zinc peroxide and its subsequent hydrolysis. Hydrogen peroxide is also formed by the action of ultraviolet light upon water:  $2\text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{H}_2$ . High anodic potentials are capable of oxidizing the oxygen in many of its compounds to the peroxide state: for example, concentrated sulfuric acid is oxidized to per-

oxydisulfuric acid  $\text{HOSOOH}$ . This acid may then be

hydrolyzed to form hydrogen peroxide and sulfuric acid. Some commercial hydrogen peroxide is prepared in this manner, but the greater portion is prepared by the action of cold sulfuric acid upon hydrated barium peroxide:  $\text{BaO}_2 + \text{H}_2\text{SO}_4 = \text{BaSO}_4 + \text{H}_2\text{O}_2$ . The peroxide being less volatile than water may be concentrated by evaporation under reduced pressure. Another method of preparation involves the formation of hydrogen peroxide as the product of the oxidation of organic hydrazo-compounds by oxygen. The hydrogen peroxide is removed by distillation and the hydrazo-compound regenerated by reduction with sodium-amalgam.

**12.** Pure hydrogen peroxide is a faint blue syrupy liquid freezing at  $-2^\circ$ . It has a vapor pressure of 47 mm. at  $80^\circ \text{C}$ . Violent decomposition occurs if heated much above this temperature. The dielectric constant of the liquid is given as 93, a value even higher than that of water. The water solutions are fairly stable if kept in a cool, dark place. Acetanilid is usually added to the commercial product to act as a preservative. The decomposition into water and oxygen,  $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ , is catalyzed by many substances, for example, silver, manganese dioxide, hydrogen bromide, and saliva. The decomposition is more rapid in alkaline solution. The usual 3 per cent commercial prepara-

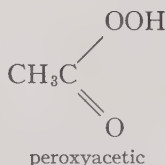
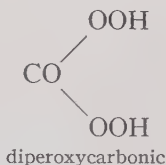
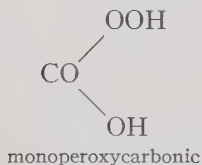
tion is often called a "10 volume solution" since it will evolve about 10 times its volume of oxygen.

Peroxide is a powerful oxidizing agent in both acid and alkaline solutions (Par. 14), the oxygen being reduced from an oxidation state of  $-1$  to  $-2$ . However, it is generally a slow oxidizing agent except with fairly powerful reducing agents. One of the most important reactions of hydrogen peroxide is the quantitative oxidation of iodide:  $2\text{I}^- + \text{H}_2\text{O}_2 + 2\text{H}^+ = \text{I}_2 + 2\text{H}_2\text{O}$ . It also acts as a reducing agent, the oxygen being oxidized from  $-1$  to  $0$ , but a fairly powerful oxidizing agent is required to bring about its oxidation in acid solution. As examples we have the quantitative reduction of permanganate:  $5\text{H}_2\text{O}_2 + 2\text{MnO}_4^- + 6\text{H}^+ = 2\text{Mn}^{++} + 5\text{O}_2 + 8\text{H}_2\text{O}$ , and the reduction of silver oxide:  $\text{Ag}_2\text{O} + \text{H}_2\text{O}_2 = 2\text{Ag} + \text{O}_2 + \text{H}_2\text{O}$ .

Hydrogen peroxide is used as an antiseptic and as a bleaching agent for hair, silk, feathers, ivory, etc.

Delicate qualitative tests for peroxide are the reactions with chromate or titanate sulfate in acid, forming highly colored peroxy-acids. The peroxychromic acid is a bright blue compound, soluble in ether, and the peroxytitanic acid is yellow.

**13. Peroxy-acids.**—There are a large number of acids containing peroxy-oxygen. These may be considered as derivatives of oxy-acids formed by the substitution of  $-\text{OOH}$  in place of  $\text{OH}^-$ , for example



The elements forming peroxy-acids are B, C, Ti, Ge, Sn, N, P, V, Cr, Ta, S, Cr, Se, Mo, W, and U. Many of these acids are discussed under the respective elements. The most important is probably peroxydisulfuric acid,  $\text{H}_2\text{S}_2\text{O}_8$ .

**14. Ozone.**—The density of ozone corresponds to the molecular formula  $O_3$ . The reaction,  $3O_2 = 2O_3$ , absorbs 34.5 kcal. per mole, and the formation of ozone from oxygen is therefore favored by high temperature. The equilibrium mixture of the gas at  $3,000^\circ C$ . probably contains about one per cent of ozone. Sufficient energy to bring about the transformation may be supplied either by ultraviolet radiation or by a silent electrical discharge. The commercial ozonizers usually consist of aluminum plates, separated by insulators, and charged to a potential of about 10,000 volts. When oxygen is passed over the plates, a few per cent of ozone is formed. Ultraviolet radiation of about  $260 \mu\mu$  (corresponding to 4.7 volts) is absorbed by oxygen molecules. These highly activated molecules then react to form ozone. The outer portion of the earth's atmosphere must contain large concentrations of ozone formed in this manner by the sun's radiation. The silent electrical discharge is the principal commercial means of forming ozone. This involves the action of electrons shot off from high-potential surfaces upon oxygen molecules. Ozone is also formed under powerful oxidizing conditions, as in the action of fluorine upon water, and by the oxidation of water by a high anodic potential, as, for example, in the electrolysis of aqueous sulfuric acid using a very high current density. The ozone molecule appears to be V-shaped and not a triangular ring as previously postulated.

Reference to the table of oxidation reduction potentials shows that ozone is itself a very powerful oxidizing agent, second only to fluorine. In the reduction in acid solution ordinarily one of the oxygens is reduced to water and the other two liberated as molecular oxygen. The gas is fairly stable toward decomposition into oxygen, and condenses to a blue liquid at  $-112.4^\circ C$ . The melting point is  $-249.7^\circ$ . It has a very pungent, characteristic odor, and unlike oxygen it is not magnetic. Ozone is more soluble in water than is oxygen, and is still more soluble in alkaline

solution. The solution contains **perhydroxyl** ion,  $\text{O}_2^-$ .



The latter is unstable in acid solution.



The potassium salt  $\text{KO}_2$  is formed by the combustion of potassium in air.

Ozone is used in sterilization of water; bleaching of paper pulp, fabrics, and flour; the resinification of oils; and as a deodorant for air in crowded interiors. (Its bactericidal properties in this connection seem not to be very great.) Qualitatively it may be detected by its peculiar odor, by its action upon potassium iodide, and by the blackening of silver.

**15. Oxidation-reduction Potentials.**—Important oxidation reduction potentials involving oxygen and its oxides have been summarized in Table III. Since the first step in the reduction of oxygen is generally the formation of the peroxide, this potential, equation (2) is an important factor in determining the action of oxygen. However the reverse reaction, that is the oxidation of water, does not involve the formation of peroxide as an intermediate step and depends upon equation (4). A tentative value is also given for the oxidation of water to free hydroxyl which may be formed as an unstable intermediate under some conditions.

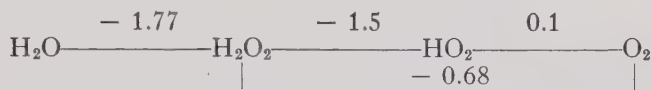
TABLE III

## OXIDATION-REDUCTION POTENTIALS

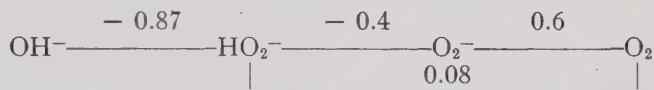
	VOLTS <sub>25°</sub>
(1) $2\text{OH}^- = \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^-$ .....	— 0.401
(2) $\text{H}_2\text{O}_2 = \text{O}_2 + 2\text{H}^+ + 2e^-$ .....	— 0.68
(3) $3\text{OH}^- = \text{HO}_2^- + \text{H}_2\text{O} + 2e^-$ .....	— 0.87
(4) $\text{H}_2\text{O} = \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^-$ .....	— 1.229
(5) $2\text{H}_2\text{O} = \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^-$ .....	— 1.77
(6) $\text{O}_2 + \text{H}_2\text{O} = \text{O}_3 + 2\text{H}^+ + 2e^-$ .....	— 2.07
(7) $\text{H}_2\text{O} = \text{OH} + \text{H}^+ + e^-$ .....	— 2.2

The potentials for the reduction of  $O_2$  in steps are given in the following scheme.

*Acidic solutions:*



*Basic solution:*



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# Chapter IV

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## GROUP I. ALKALI METALS

1. The first group of the periodic system contains the elements lithium, sodium, potassium, rubidium, and cesium. They are called the alkali metals because their hydroxides are all soluble bases or alkalies. The most important common characteristics of these elements are the single electron in the outermost energy level of their atoms, and the comparatively low voltage required to detach this electron from the atom, as shown by the ionizing potentials given in Table I.

Although the outer electron is easily removed, the underlying ones can be removed only by very high potentials; hence ordinary chemical reactions involve the loss or transfer of only a single electron per atom, as illustrated by the equation:  $M = M^+ + e^-$ . Accordingly these elements display invariably an oxidation state of +1 in their compounds.

2. **Atomic and Physical Properties.**—Many of the physical and chemical properties of these elements may be correlated with the structures of their atoms. (Cf. Table I, also *Prin. of Chem.*, Chap. XVII.) Thus in the solid state the electrons are held so loosely that they can readily pass from association with one atom to another under the impulse of an electric potential; hence these elements show in a high degree the conductivity and other properties characteristic of metals. Moreover, since there are not enough outer electrons to serve to bind an atom firmly to all of its



neighbors in the solid state, we find these metals to be soft, and easily fusible.

TABLE I  
ATOMIC AND PHYSICAL PROPERTIES

ELEMENT	LITHIUM	SODIUM	POTASSIUM	RUBIDIUM	CESIUM
Latin name.....	Lithium	Natrium	Kalium	Rubidium	Cesium
Symbol.....	Li	Na	K	Rb	Cs
Atomic weight.....	6.94	22.997	39.096	85.48	132.91
Atomic number.....	3	11	19	37	55
Melting point ° C.....	179	97.5	63.5	39.0	28.4
Boiling point ° C.....	1372	892	774	679	690
Density 20° C.....	0.53	0.97	0.86	1.53	1.90
Stable isotopes.....	6, 7	23	39, (40), 41	85, (87)	133
Nucleus {	Neutrons...	12	20, 21, 22	48, 50	78
	Protons (+)	11	19, 19, 19	37, 37	55
Electrons in various quantum levels,					
1st.....	2	2	2	2	2
2nd.....	1	8	8	8	8
3rd.....	—	1	8	18	18
4th.....	—	—	1	8	18
5th.....	—	—	—	1	8
6th.....	—	—	—	—	1
Ionizing potentials of gaseous atoms, volts,	5.36	5.12	4.32	4.16	3.87
Potential required to remove electrons from solid metal . . .	2.35	2.12	—	—	—
Potential between metal and normal aqueous soln. of ion; $M = M_{aq}^{+} + e^{-}$ . . .	3.02	2.71	2.92	2.99	3.02
Heat of hydration of gaseous ions, kcal....	123	97	77	70	63
Ionic radius in crystals, cm. $\times 10^8$ .....	0.60	0.95	1.33	1.48	1.69

Another phenomenon connected with the easy loss of electrons by these metals is their solubility in liquid ammonia to give highly conducting solutions. The process of solution is accompanied by an ionization of the metal atom whose electron attaches itself to a molecule of ammonia; thus,  $M$  (solid) =  $M^{+}$  (in  $NH_3$ ) +  $e^{-}$  (ammoniated). The alkali metals all give solutions in ammonia of the same blue color, which is due to the solvated electron, the metal ion being colorless in all cases. The addition of  $MCl$  increases

the concentration of  $M^+$  and diminishes the blue color in accordance with the mass law. The alkaline earth metals are soluble in liquid ammonia in this way to a smaller extent, and the nobler metals, which hold their electrons more firmly, do not dissolve at all in liquid ammonia.

The metal vapors are somewhat associated into diatomic molecules at the boiling points of the liquids. The heats of dissociation of the  $Na_2$  and  $K_2$  molecules are 18,000 and 12,000 cal. respectively.

The nuclei of potassium, 40, and rubidium, 87, are not altogether stable, as shown by their slight radio-activity (cf. XXII—16).

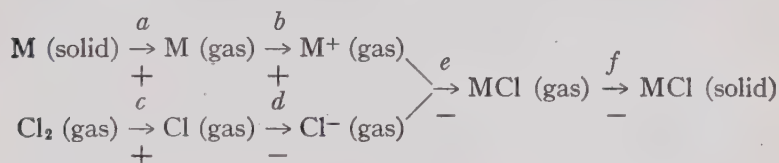
**3. Spectra.**—Spectra of the alkali metals are easily excited; even the comparatively low temperature of a Bunsen flame suffices to disturb the outer, valence electron; moreover, since the single valence electron alone is disturbed, unless a high voltage spark is used, their spectra are comparatively simple. The wave length (in mm.  $\times 10^{-6}$ ) of the prominent lines in the flame spectra are as follows: lithium, 670 red, 620 orange, fainter; sodium, 590 yellow; potassium, 768 red, 404 violet; rubidium, 780 red, 420 blue, 358 violet; cesium, 457 blue, 388 violet.

**4. Chemical Properties.**—Since the metals all give up their outer electrons so easily to other substances they are chemically very reactive. Thus, they all decompose water vigorously, the water taking up the electrons and giving hydroxide ion and hydrogen gas:  $M \text{ (solid)} + H_2O = \frac{1}{2}H_2 + M^+ + OH^-$ . With potassium, rubidium, and cesium the amount of heat developed is so great that the metal takes fire almost instantly when thrown upon water.

**5.** The ease with which an electron is removed from the metal increases regularly in going from lithium to cesium, as shown by the ionizing potentials; hence we would expect that the ease with which the metal forms any one of its compounds would increase from lithium to cesium; and, conversely, the difficulty of reducing the metal from its

compounds would be greatest for cesium and least for lithium. This is in general the case, although the simple prediction is somewhat modified by the different sizes and attractions of the resulting ions. The ionizing potentials refer to the reaction:  $M(\text{gas}) = M^+(\text{gas}) + e^-(\text{gas})$ , while the reaction between solid metal and water, previously given, involves in addition the hydration of the  $M^+$ . This sets free a large amount of energy, and just as the smallest ion, lithium, attracts an electron most strongly, so also it attracts water molecules most strongly, a fact which helps lithium metal to react with water to give it a high electrode potential in water solution, as shown in Table I, instead of the lowest as one would conclude from the ionizing potentials alone.

This point may be clarified by the aid of the following scheme representing the formation of  $MCl$  by a series of steps, which give out or absorb energy, as the case may be.



We have marked each step  $+$  in which the system would absorb heat, and each  $-$  in which the system would lose heat. If potassium were substituted for lithium, steps  $c$  and  $d$  would naturally remain the same; step  $a$  would become smaller (Table I) showing that potassium is more easily fused and vaporized; step  $b$  would have a smaller positive value (see Ionizing Potentials); but step  $e$  would also have a smaller negative value, the last two effects thus tending to offset each other. Although the heats evolved in formation per mole follow for most compounds the order expected from the ionizing potentials, and illustrated by the iodides, bromides, and chlorides in Table II, the fluorides show the reverse order on account of the small size of the

lithium and fluoride ions, allowing close approach and a large negative value for step  $e$ .

TABLE II  
HEATS EVOLVED IN FORMATION OF ALKALI HALIDES,  
KILOGRAM CALORIES PER MOLE

	Li	Na	K	Rb	Cs
Iodides .....	71	76	85	88	90
Bromides .....	87	90	97	99	101
Chlorides .....	97	99	105	105	106
Fluorides .....	145	137	135	133	132

For the same reason, the compounds with other small atoms usually show the greatest stability with lithium rather than with cesium. Other examples include the hydrides, carbides, nitrides, and oxides.

The smaller size and larger ionizing potential of lithium tends to ally it somewhat with the elements of Group II, particularly magnesium. This is in harmony with the corresponding resemblance between beryllium and aluminum, boron, and silicon. This resemblance is illustrated by the low solubility of its carbonate and phosphate, as well as by the stability of the compounds mentioned in the preceding paragraph.

6. The complete transfer of electrons by the alkali metals in the formation of their compounds is illustrated again by the crystal structure of their halides. All except those of cesium crystallize in a cubic lattice of the sodium chloride type (Append. V; cf. also CsCl type) in which the sodium and chlorine atoms alternate, and each atom of one kind is surrounded by six atoms of the other, *all equidistant from it*. It is not possible to designate any sodium atom as belonging to any particular chlorine atom. There are, therefore, no molecules of NaCl present in the crystal. Now if each sodium atom retained its original electron it would be bound (by an electron pair) to a particular chlorine atom; the absence of such binding shown by the symmetry of the

crystal lattice is evidence that the electrons have passed over to the chlorine atoms, giving each an extra electron, making it chloride ion,  $\text{Cl}^-$ , and leaving the sodium atom as sodium ion,  $\text{Na}^+$ . Indeed, we have only to melt the crystal, releasing these ions from their fixed positions, and the substance becomes an excellent electric conductor, quite unlike a substance such as sulfur, which is an insulator in the liquid as well as the solid form. The solution of an alkali halide in water merely substitutes the attraction of its ions for water for their attraction for each other. The energy of hydration is very high (Table I) and serves to overcome the large electrostatic force responsible for the cohesion of the crystal.

The fact that lithium has the largest energy of hydration is noteworthy in connection with the high solubility of many of its salts. The salts of low solubility are those where there is an especially high attraction between the lithium ion and the negative ion in the crystal, as in the case of the fluoride.

**7. Occurrence.**—From the average composition of igneous rocks, the percentage of the alkali metals present is estimated as, sodium 2.85, potassium 2.60, lithium  $4 \times 10^{-5}$ , and rubidium  $10^{-6}$  and cesium  $10^{-7}$ . Spectral lines of lithium and sodium are prominent in the sun. The spectra of the other alkalies are not found in the chromosphere of the sun doubtless because the temperature is sufficient to remove the outer electron completely. Potassium and rubidium can, however, be observed in the cooler portions.

Sea water contains about 2.8 per cent of sodium chloride and 0.08 per cent of potassium chloride, and the evaporation of inland seas has resulted in enormous deposits of these salts. These deposits of chlorides, and also deposits of carbonates, sulfates, and nitrates are discussed under the corresponding salts. Most plants contain from 4 to 6 times as much combined potassium as sodium, a fact responsible for the use of potassium compounds as one of the important fertilizers. The ashes of sea weeds, however, contain more

TABLE III

SUMMARY OF THE MORE IMPORTANT REACTIONS OF THE ALKALI METALS

$4M + O_2 = 2M_2O$	Li only
$2M + O_2 = M_2O_2$	Li slightly, Rb and Cs spontaneously in dry air
$M + O_2 = MO_2$	K, Rb, Cs
$6M + N_2 = 2M_3N$	Li only
$2M + X_2 = 2MX$	With halogens
$2M + S = M_2S$	With Te also
$3M + P = M_3P$	With As, Sb also
$2M + 2H_2O = 2M^+ + 2OH^- + H_2$	
$2M + 2C_2H_5OH = 2C_2H_5OM + H_2$	
$2M + 2NH_3 \text{ (gas)} = 2NH_2M + H_2$	
$3M + AlCl_3 = 3MCl + Al$	At high temperature
$6M + B_2O_3 = 3M_2O + 2B$	At high temperature
$2M + H_2 = 2MH$	
$5M + MnO_3 = 3M_2O + \frac{1}{2}N_2$	

sodium than potassium carbonate, with certain exceptions. The alkalis are found in varying amounts in nearly all silicates. The three commercially important lithium minerals are: amblygonite,  $LiAlFPO_4$ ; spodumene,  $LiAl(SiO_3)_2$ ; and lepidolite,  $Li_2[F, OH]_2Al_2(SiO_3)_2$ . The principal source of cesium is the mineral pollucite,  $H_2Cs_4Al_4(SiO_3)_9$ . Potassium feldspar,  $KAlSi_3O_8$ , is a constituent of granite.

**8. Preparation and Uses of the Metals.**—Lavoisier, in 1793, predicted that the "alkalies" would prove to be metallic oxides. Sir Humphry Davy isolated sodium and potassium in 1807 by electrolysis of their hydroxides. This method is today the one used in the technical preparation of sodium. The metals may also be prepared by the reduction of the hydroxide or carbonate at moderately high temperatures, with iron, calcium, carbon, or other reducing agents. The reduction by less electropositive elements is accomplished through the greater volatility of the alkali metals. The reduction with calcium furnishes probably the simplest laboratory method of preparing rubidium and cesium.

Many attempts have been made to prepare sodium by the electrolysis of the fused chloride, but the mechanical difficulties arising from the corrosive action of the molten chlo-



ride and hot chlorine have been too great for successful operation. The Castner process, which is now in general use, employs the fused hydroxide at a temperature slightly above its melting point. Both hydrogen and alkali metal are liberated at the cathode. The liquid metal floats to the surface of the molten hydroxide, where it is protected from oxidation by the atmosphere of hydrogen which is maintained, whence it is drawn off from time to time. A small amount of lithium is manufactured by the electrolysis of a fused mixture of lithium and potassium chloride.

The only one of these metals to find any considerable commercial use is sodium. The most important of its uses are the manufacture of sodium peroxide and cyanide, lead tetraethyl, and in the preparation of organic chemicals and dyes where a powerful reducing agent is required. The manufacture of photoelectric cells consumes some cesium but the amount required per cell is small.

**9. Alloys.**—Sodium amalgamates with mercury with almost explosive violence. The amalgam is often used in place of the solid metal as a reducing agent. An alloy of 24 per cent sodium and 76 per cent potassium is liquid down to  $-12.6^{\circ}$ . This is sometimes used to remove traces of water from gases. Lithium is more like the elements of the second and third groups (Par. 25) and therefore alloys with them more readily than do sodium or potassium. Its alloy with aluminum may achieve commercial importance on account of its very low density. A lithium lead alloy is used for cable sheath, and small amounts of lithium are sometimes added to copper alloys as a "deoxidizer."

**10. Hydrides.**—Compounds of the type MH are formed by the direct action of hydrogen upon the heated metals. These compounds are salt-like in appearance and are of interest because of their analogy to the alkali halides. The electrolysis of the molten hydride results in the liberation of hydrogen at the anode, indicating that the hydrogen possesses a negative charge. Sodium and potassium hy-

dride react with carbon dioxide, forming sodium formate:  
 $\text{NaH} + \text{CO}_2 = \text{HCOONa}$ .

**11. Oxides.**—The direct action of oxygen upon lithium produces the monoxide,  $\text{Li}_2\text{O}$ , and a trace of lithium peroxide,  $\text{Li}_2\text{O}_2$ ; with sodium the peroxide,  $\text{Na}_2\text{O}_2$ , is produced; and with potassium, rubidium, and cesium the oxide,  $\text{MO}_2$  results. The monoxides cannot be prepared by dehydration of the hydroxides, but may be formed by the action of the metal upon the nitrate, e.g.  $5\text{K} + \text{KNO}_3 = 3\text{K}_2\text{O} + \frac{1}{2}\text{N}_2$ . The oxides of the type,  $\text{M}_2\text{O}_2$ , are salts of hydrogen peroxide, while the type  $\text{MO}_2$  are derivatives of the unstable compound  $\text{HO}_2$  (cf. III—14). The only oxide of commercial importance is  $\text{Na}_2\text{O}_2$  which is used extensively as a source of oxygen and hydrogen peroxide under the name of "oxone." The peroxide hydrolyzes in water with the formation of  $\text{H}_2\text{O}_2$ . When a small amount of water is used upon an excess of sodium peroxide, the liberated hydrogen peroxide decomposes with evolution of oxygen. Sodium peroxide is made commercially by heating sodium in dry air free from carbon dioxide to a temperature somewhat above  $300^\circ$ . The principle of counter currents is employed.

**12. Hydroxides.**—The older methods of manufacture used the reaction between a dilute solution of the alkali carbonate and milk of lime.  $2\text{Na}^+ + \text{CO}_3^{--} + \text{Ca}^{++} + 2\text{OH}^- = \text{CaCO}_3 + 2\text{Na}^+ + 2\text{OH}^-$ . Half of the hydroxide consumed in this country is produced by this process. The balance is manufactured by the electrolysis of a solution of the alkali chloride, a process which results in the formation of the hydroxide and hydrogen at the cathode and chlorine at the anode. The cell reaction is:  $2\text{H}_2\text{O} + 2\text{Cl}^- = 2\text{OH}^- + \text{H}_2 + \text{Cl}_2$ . In carrying out this electrolysis the cell must be constructed so as to prevent the interaction of the hydroxide and the chlorine, which would give hypochlorite at low temperatures or chlorate at higher temperatures. This problem is not altogether easy since the hydroxide moves toward the anode under the electric

field and the chlorine is somewhat soluble in the brine. The **Nelson** cell used most extensively in the United States, has a carbon anode and perforated steel cathode. The brine percolates through the cell and out of the perforations in the cathode at such a rate that the hydroxide is swept back and prevented from reaching the anode. The liquid coming from the cell contains a mixture of the hydroxide and chloride. Upon evaporation the greater portion of the chloride is precipitated.

The **Castner-Kellner** process takes advantage of the fact that sodium or potassium may be electrolyzed from a concentrated brine solution with a mercury cathode to form a dilute amalgam, and this amalgam will react with water to form a dilute hydroxide solution. The cell employed is in-

TABLE IV  
PRODUCTION AND CONSUMPTION OF SODIUM COMPOUNDS  
IN UNITED STATES IN 1938

PRODUCTION OF SODIUM COMPOUNDS		CONSUMPTION OF SODIUM CARBONATE	
	<i>Tons</i>		<i>Tons</i>
Chloride.....	9,000,000	Glass.....	650,000
Carbonate.....	2,800,000	Soap.....	220,000
Hydroxide.....	900,000	Chemicals.....	600,000
Silicate.....	600,000	Cleaning compounds.....	125,000
Sulfate.....	300,000	Paper.....	90,000
Bicarbonate.....	140,000	Water softening.....	40,000
Borate.....	150,000	Petroleum.....	12,000
Phosphate.....	125,000	Textiles.....	35,000
Chromate.....	45,000		
Thiosulfate.....	35,000	CONSUMPTION OF SODIUM HYDROXIDE	
Sulfide.....	30,000		<i>Tons</i>
Sulfite.....	15,000	Soap.....	100,000
Hypochlorite.....	12,000	Chemicals.....	140,000
Nitrate.....	3,000	Petroleum.....	95,000
Fluosilicate.....	5,000	Rayon.....	170,000
Fluoride.....	1,000	Lye.....	45,000
Metal.....	10,000	Exports.....	100,000
Acetate.....	3,000	Textiles.....	40,000
Benzoate.....	600	Rubber reclaiming.....	10,000
Citrate.....	1,500	Pulp and paper.....	40,000
		Vegetable oils.....	17,000

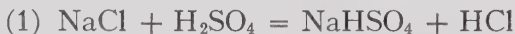
geniously constructed for the continuous operation of these reactions. The process gives a very pure product.

Commercial sodium and potassium hydroxides may contain, in addition to large amounts of chloride, some carbonate, sulfate, nitrate, phosphate, acetate, and peroxide, as well as small amounts of the other alkalis. The hydroxide, sold as "pure by alcohol," has been dissolved in alcohol which separates out most of the impurities, but leaves a little chloride, carbonate, and acetate. A hydroxide free from the negative impurities may be made by treating a solution of purified alkali carbonate with silver carbonate and boiling the resulting solution with carefully purified lime in a silver dish.

The consumption of sodium hydroxide in the more important industries is given in Table IV. Potassium hydroxide is used less extensively than the sodium compound because of its greater cost. Its principal use is in the manufacturing of soft soap, which owes its properties to the greater solubility of the potassium compound.

**13. Sodium Carbonates and Bicarbonates.**—Sodium carbonate is found in high concentration in the lakes of many arid regions. Mono Lake and Owen's Lake in California contain millions of tons capable of rather cheap extraction.

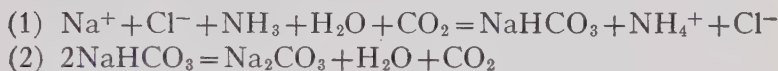
The ashes of certain sea plants were formerly the common source of the salt, but it is now manufactured from sodium chloride. The **Le Blanc process** was the earliest (1791) method employed on a large scale for the conversion of chloride to carbonate, but the method is rapidly becoming obsolete. The steps in the process are:



Reaction (1) occurs readily upon gentle heating, but reaction (2) requires a much higher temperature. The third

and fourth steps are carried out in a rotary furnace at a temperature of  $700\text{--}1,000^\circ$ , the charge consisting of a mixture of the sodium sulfate with coal dust and limestone. The product, called "black ash," is extracted with water and impure carbonate,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , obtained by crystallization. The sulfide residue is usually oxidized to free sulfur and thus made a profitable by-product.

The **Solvay** or **ammonia** process has now largely superseded the Le Blanc. It is based upon the reactions:



Reaction (1) depends upon the slight solubility of sodium bicarbonate in the solution at a temperature of  $15^\circ \text{C}$ . or below. The reaction is carried out by first saturating the brine with ammonia, and then with carbon dioxide. Following this the solution is cooled and the bicarbonate removed by filtration. Reaction (2) takes place upon gentle ignition.

The success of the process depends upon the recovery of the ammonia by the reaction:  $2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 = 2\text{NH}_3 + \text{CaCl}_2 + 2\text{H}_2\text{O}$ . Limestone serves as the source of both the carbon dioxide and the lime:  $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$ .

The phase relations of the various hydrates are indicated in Fig. 1. The an-

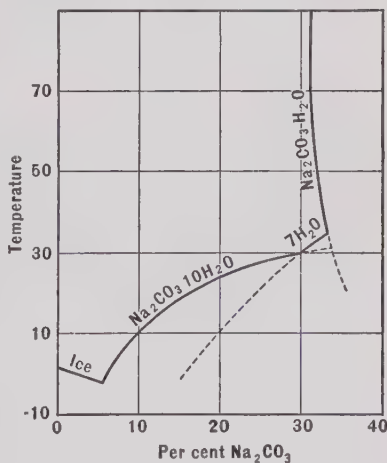


FIG. 1. The system sodium carbonate and water.

hydrous salt is known commercially as **soda-ash** and the decahydrate as **washing soda**. As the salt of a weak acid, sodium carbonate is hydrolyzed in solution,  $1N \text{Na}_2\text{CO}_3$

containing about  $0.01N$   $OH^-$ ; and many of its uses, such as washing, depend upon this property. As a salt of a weak acid, it is also used to neutralize strong acids and in the preparation of their sodium salts. The consumption of sodium carbonate by various industries is given in Table IV.

Sodium bicarbonate, the common household baking soda, is obtained as a step in the Solvay process. With the excep-

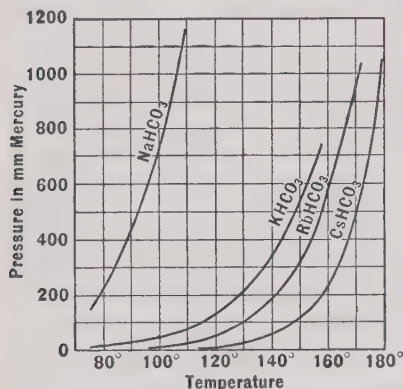


FIG. 2. Decomposition pressures of alkali bicarbonates.

tion of lithium, the alkali bicarbonates are all more insoluble than the carbonates. The conversion of bicarbonate to carbonate by heating becomes more difficult the higher the atomic weight of the alkali, as is indicated in the plot of decomposition pressures (Fig. 2). Advantage may be taken of the reversible reaction,  $CO_3^{2-} + CO_2 + H_2O = 2HCO_3^-$ , to con-

vert carbonates into bicarbonates. When a bicarbonate solution is evaporated at  $100^\circ$  or above, sodium sesquicarbonate,  $Na_3(CO_3)(HCO_3) \cdot 2H_2O$  separates.

The bicarbonate is employed in baking, the use depending upon the liberation of carbon dioxide with acid, as does also its use in certain types of fire extinguishers. The ease of purification of sodium bicarbonate by crystallization renders it a valuable standard in the titration of acids and bases. For this use it is fused to convert to the carbonate and to remove the last traces of water. This operation should be carried out in an atmosphere of  $CO_2$ , since the decomposition pressure of  $Na_2CO_3$  is 2.2 mm. at  $700^\circ$  and 6.2 mm. at  $1,000^\circ$ .

**14. Potassium Carbonates.**—For centuries potassium carbonate was extracted from wood ashes; hence its name,



potash. It may be made from the chloride by the Le Blanc process, but not by the Solvay process, since the bicarbonate is not sufficiently insoluble. However the conversion is generally carried out: (1) by the precipitation of  $\text{KHCO}_3 \cdot \text{MgCO}_3 \cdot 4\text{H}_2\text{O}$  by passing  $\text{CO}_2$  under pressure into a suspension of  $\text{MgCO}_3$  in  $\text{KCl}$  solution and (2) the recovery of the potassium carbonate from the double salt by decomposition with hot water giving insoluble  $\text{MgCO}_3$  and a solution of potassium carbonate,  $2\text{MgKH}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O} = 2\text{MgCO}_3 + \text{K}_2\text{CO}_3 + \text{CO}_2 + 9\text{H}_2\text{O}$ . Other sources are the mother liquors obtained in the manufacture of beet sugar, wine-lees, and water used in washing crude wool which contains potassium fatty acids. In each case the organic material is ignited to give the carbonate.

Potassium carbonate crystallizes as the dihydrate. It is used in making soap and hard glass, and in the textile industries.

Potassium bicarbonate is similar in chemical properties to the sodium salt but is about three times as soluble.

**15. Lithium, Rubidium, and Cesium Carbonates.**—Lithium carbonate is the most important commercial compound of that element, is used in medicine, in the preparation of other lithium compounds, in ceramics for producing high glazes, and in the glass industry for making special glasses with high fluidity when molten. Its solubility is sufficiently low so that it may be prepared by precipitation from a solution containing lithium ion by the addition of sodium carbonate. Lithium bicarbonate is soluble.

The rubidium and cesium carbonates and bicarbonates resemble the potassium compounds.

**16. Fluorides.**—The alkali fluorides do not occur free in nature to any large extent, although sodium aluminum fluoride,  $\text{Na}_3\text{AlF}_6$ , cryolite, occurs in large deposits. The fluorides are usually prepared by the action of hydrofluoric acid upon the carbonate. With excess of the acid they tend to form acid fluorides such as  $\text{MHF}_2$  or even  $\text{MH}_3\text{F}_4$

(cf. X—10). These acid compounds are sometimes used as a method of preparing pure hydrogen fluoride, since they readily decompose with the evolution of the gas. Lithium fluoride is but slightly soluble. Sodium fluoride has some use as an insecticide and a wood preservative. It is also used in the preparation of complex fluorides.

**17. Chlorides.**—Alkali chlorides are found in great deposits resulting from the evaporation of inland lakes or seas.

**Sodium chloride.** In many places great beds of almost pure sodium chloride have been located and from these salt is taken by ordinary mining operations. In regions removed from naturally occurring salt deposits, sodium chloride is obtained from sea water or salt wells usually by solar evaporation in shallow ponds. Crude salt generally contains traces of calcium and magnesium chlorides which are objectionable because of their deliquescence. Pure sodium chloride may be precipitated from a concentrated brine upon addition of hydrogen chloride gas, due, in part, to the increase in concentration of chloride ion. The reaction qualitatively is that predicted

by the Mass Law.

The solubility of sodium chloride changes but slightly with temperature, being 26.3 per cent at 0° and 28.1 per cent at 100°. Phase relations in the salt-water system are given in Fig. 3. The crystal structure has been discussed in Paragraph 6.

The production of salt in the United States in 1938

was about nine million tons. Of this three million tons were used in the preparation of the carbonate by the Solvay process. Other important industrial uses include refrigera-

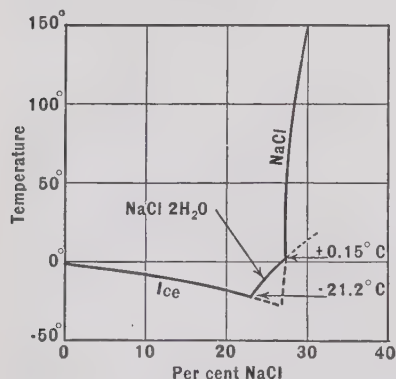


FIG. 3. The system sodium chloride and water.

tion; agriculture; household; metallurgy of silver, copper, and lead; tanning; preservative; ceramics; salting out of soap; preparation of hydrochloric acid and sodium sulfate by reaction with sulfuric acid; and the preparation of sodium hydroxide and chlorine by electrolysis.

**18. Potassium Chloride.**—For many years Germany enjoyed an almost complete monopoly of potassium salts through the possession of the extensive deposits of chloride at Stassfurt in Prussia. Since 1930 there has occurred a rapid development of the potash deposits in the United States. These have been principally the deep lying saline deposits in New Mexico and the natural brines of Searles Lake in California. About a half million tons of potassium salts, chiefly chloride, were produced from these sources in 1938. This constituted somewhat more than half of the American consumption.

The major portion of the potassium chloride of the Stassfurt deposits is in the form of double salts of magnesium and calcium chloride, sulfate, and borate. The most important of these is carnallite,  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ , and to a lesser extent kainite,  $\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$ . Potassium chloride is extracted by dissolving carnallite in hot magnesium chloride solution; cooling this solution precipitates the greater part of the potassium chloride. The yearly production of potassium chloride at Stassfurt is in excess of 1,500,000 tons. The dust from blast furnaces manufacturing pig iron, and the dust from cement kilns, has been shown to contain potassium chloride and also sulfate in recoverable amounts. It is estimated that the United States could produce several hundred thousands of tons yearly from this source. The most important uses of the potassium chloride are as fertilizer (about 90 per cent) and in the production of potassium hydroxide and other potassium compounds.

**19. Lithium, Rubidium, and Cesium Chlorides.**—Lithium chloride is the most soluble of the group. It forms mono-,

di-, and tri-hydrates, and in many respects resembles magnesium chloride.

One of the most important sources of rubidium and cesium chlorides is the mother liquor remaining after the extraction of the potassium chloride from carnallite. These elements are usually separated from the liquid by conversion into the relatively insoluble alums through the addition of aluminum sulfate.

**20. Bromides and Iodides.**—Bromides and iodides occur in sea water and in the various salt deposits. They are not recovered as such, but the halogens are liberated as the free elements, and the salts prepared from the elements by methods discussed under the halogens. Sodium and potassium bromides are used in medicine as sedatives, and in photography for precipitating silver bromide and as retardants in developers. The alkali iodides find limited application in photography, and in medicine to supply iodine to the thyroid gland, and sometimes in tincture of iodine, to increase the amount of iodine that can be dissolved.

**21. Cyanides.**—Sodium cyanide is made on a large scale from sodium amide (Table III) by reduction with carbon at red heat:  $\text{NaNH}_2 + \text{C} = \text{NaCN} + \text{H}_2$ . A mixture of sodium and potassium cyanides may be prepared by the reduction of potassium ferrocyanide with sodium:  $\text{K}_4\text{Fe}(\text{CN})_6 + 2\text{Na} = 4\text{KCN} + 2\text{NaCN} + \text{Fe}$ . Potassium cyanide is also manufactured by the action of ammonia upon a mixture of potassium carbonate and carbon at a high temperature:  $\text{K}_2\text{CO}_3 + 2\text{NH}_3 + 4\text{C} = 2\text{KCN} + 3\text{CO} + 3\text{H}_2$ . The alkali cyanides are very soluble in water, and the solution is quite alkaline due to the hydrolysis of the cyanide. The uses of these compounds in gold mining and electroplating depend upon the formation of complex cyanides with gold, silver, and platinum. The sodium salt is now generally used due to the fact that it is cheaper and gives a higher weight of cyanide per pound of salt. Like all substances giving

cyanide ion or hydrogen cyanide in solution, these salts are very poisonous.

**22. Sulfates.**—The alkali sulfates and double sulfates with calcium and magnesium are found in the various salt lakes and salt deposits. Double sulfate of sodium and potassium, as  $\text{KNaSO}_4$ , and various types of sodium and potassium alums are of frequent occurrence in volcanic lava. Sodium sulfate, called salt cake, is a product of the manufacture of hydrochloric acid from sodium chloride. Some potassium sulfate is extracted from the Stassfurt deposits.

Sodium sulfate is used in medicine as a cathartic and in the manufacture of cheap glass to furnish the sodium. Its principal use (over 200,000 tons annually) is in the "sulfate" process for the manufacture of wood pulp. It can be crystallized as  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , Glauber's salt, below  $32.384^\circ$ , and as the anhydrous sulfate above that temperature. The transition point serves as a convenient "fixed point" in the standardization of thermometers. The solubility of the decahydrate increases rapidly with temperature and the solutions formed at the higher temperatures may be readily cooled in the supersaturated state. If a particle of this solid hydrate is then added, crystallization takes place and the whole solution appears to solidify. An unstable heptahydrate may be crystallized out below  $24^\circ \text{C}$ . Potassium sulfate is used in the preparation of potassium alum and also as fertilizer, being preferred to the chloride for this purpose with certain crops, especially tobacco.

**23. Nitrates.**—Alkali nitrates are formed in nature through the decomposition of organic material. Due to the solubility of these salts, deposits are found only in the rainless regions of the earth. By far the most important occurs in Chile, and is composed chiefly of sodium nitrate. Commercial "Chile saltpetre," consisting of 95 to 98 per cent sodium nitrate, is made by extracting the crude nitre rock with water. Chile saltpetre was formerly almost the only source of the nitric acid and nitrate-fertilizer, but now has

been largely replaced by the various processes for the fixation of atmospheric nitrogen (cf. **XII—32**).

The uses of the alkali nitrates which depend upon the oxidizing power of nitrate are discussed under the chemistry of nitrogen. Potassium nitrate absorbs water less readily than sodium nitrate, and for this reason was formerly used more extensively than the sodium salt in gunpowder. Potassium nitrate is prepared from the sodium by double decomposition with potassium chloride, taking advantage of the fact that the solubilities of potassium chloride, potassium nitrate, and sodium nitrate increase rapidly with temperature, while that of sodium chloride is hardly affected. The sodium nitrate is dissolved in hot water and concentrated potassium chloride solution is added, whereupon most of the sodium is precipitated as chloride. The solution is then evaporated, more sodium chloride first separating, followed by potassium nitrate.

The crystal structure of sodium nitrate is similar to the simple cubic arrangement of sodium chloride (Par. 6), the nitrate group as a whole occupying the positions corresponding to the chloride ion. The alkali nitrates differ from the nitrates of most of the other metals in that upon heating they first decompose into nitrite and oxygen. Upon further heating nitrogen and oxygen are evolved and the oxide and peroxide formed. A mixture of 45 per cent sodium and 55 per cent potassium nitrates melts at  $220^{\circ}$  and is a convenient high temperature liquid bath.

**24. Other Salts of the Alkali Metals.**—Compounds of the alkali metals with sulfide, thiosulfate, chlorate, perchlorate, phosphate, borate, and silicate are of importance, but since their properties and uses depend so largely upon the chemistry of negative ions, they are discussed in the chapters dealing with those ions.

**25. Chemical and Analytical Properties of Ions.**—The outstanding characteristic of the alkali ions is the slight tendency to form insoluble salts or complex ions. As already



mentioned, lithium resembles the alkaline earth metals in many respects. Thus lithium fluoride, carbonate, and phosphate are moderately insoluble and the bicarbonate more soluble than the carbonate, like the alkaline earth metals, and unlike the rest of the alkalis. Lithium ion is slightly hydrolyzed. The chloroplatinates, acid tartrates, and alums of lithium and sodium are soluble, while the corresponding salts of potassium, rubidium, and cesium are relatively insoluble. Potassium forms with sodium cobaltinitrite in dilute acid the precipitate,  $K_2NaCo(NO_2)_6$ . It is the least soluble of the potassium compounds, but this does not serve to distinguish potassium from rubidium, cesium, or ammonium, which form corresponding compounds. Potassium picrate,  $C_6H_2(NO_2)_3OK$ , potassium perchlorate,  $KClO_4$ , and sodium and potassium fluosilicates,  $Na_2SiF_6$ ,  $K_2SiF_6$ , are also but slightly soluble. Sodium antimonate,  $NaSb(OH)_6$ , is the least soluble of the sodium salts. Sodium may be precipitated from solutions containing potassium by use of the uranyl zinc acetate reagent. The formula of the precipitate is  $NaZn(UO_2)_3Ac_9 \cdot 6H_2O$ . For quantitative determinations the conditions for the precipitation must be carefully controlled.

Potassium ion appears to be more readily absorbed than sodium ion, and this in part accounts for the much smaller quantity of potassium salts in sea water, although another factor may be its more ready precipitation as an iron silicate,  $KFeSi_2O_6$ .

In the quantitative analysis of the alkalis, they are usually converted to the chlorides and the mixture weighed. The lithium chloride may be extracted by dissolving in amyl alcohol. Potassium, rubidium, and cesium are converted to the chloroplatinates, and the sodium obtained by difference. Although rubidium and cesium are rarely present in quantity they may be separated from potassium by taking advantage of difference in solubility of the acid tartrates.

In addition to the use of the spectroscope in the identifica-

tion of the alkalies, advantage is taken of the color imparted to the Bunsen flame by the presence of volatile compounds of these elements. Lithium colors the flame red, sodium yellow, potassium violet, rubidium bluish red, and cesium blue. The sodium flame test is of extraordinary delicacy, being capable of detecting  $10^{-10}$  grams of sodium. Since this quantity of sodium is present in practically every substance, it is necessary in making a flame test for sodium to judge the amount of sodium present largely by the length of time that the intense yellow color persists in comparison to pure sodium chloride as a standard. The potassium flame test is about five thousand times less sensitive than the sodium test. In the presence of any considerable amount of sodium it is necessary to use a thick blue glass to cut out the yellow sodium light in order to detect the potassium.

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# Chapter V

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## GROUP II. ALKALINE EARTH METALS

1. On the basis of their atomic structure the elements with two valence electrons may be divided into a main group consisting of beryllium (formerly often called glucinium from the sweet taste of some of its compounds), magnesium, calcium, strontium, barium, and radium, and a subgroup, zinc, cadmium, and mercury. As a common characteristic the main group elements have kernels with the same number and arrangement of electrons as the preceding noble gas, while the subgroup elements have kernels with eighteen electrons in the outer shell. Beryllium and magnesium are smaller and much less basic than the rest of the main group, and before the fundamental differences in atomic structure were recognized, they were frequently classified with the subgroup elements. The remaining elements of the main group have hydroxides with distinctly alkaline properties and have long been known as the alkaline earth elements, and we shall use the term as applying to all of the main group.

2. **Physical Properties of Metals.**—The elements in the free state are highly metallic. They have grey white luster when freshly cut, but readily tarnish, especially the heavier members of the group. Although somewhat brittle, they may be hammered and rolled. Beryllium is hard enough to scratch glass, while barium is but slightly harder than lead. The metals are good electrical conductors; the specific conductivity of calcium is about 45 per cent that of silver.

Their melting points (Table I) are much higher than those of the alkali metals.

TABLE I  
ATOMIC AND PHYSICAL PROPERTIES OF ALKALINE EARTH ELEMENTS

	Be	Mg	Ca	Sr	Ba	Ra
Atomic number.....	4	12	20	38	56	88
Atomic weight.....	9.02	24.32	40.8	87.63	137.36	226.05
Isotopes.....	9, (8)	24, 25, 26	40, 44, 42, 43, 46, 48	88, 86, 84, 87, 90	138, 136, 134, 137, 135, 132	224, 226
Electrons in various quantum levels, 1st.....	2	2	2	2	2	2
2d.....	2	8	8	8	8	8
3d.....		2	8	18	18	18
4th.....			2	8	18	32
5th.....				2	8	18
6th.....					2	8
7th.....						2
Ionic radius $\times 10^8$ cm.....	0.31	0.65	0.99	1.13	1.35	
Ionization potential of gaseous atom, volts,						
1st electron.....	9.28	7.61	6.09	5.67	5.19	5
2d electron.....	18.1	14.96	11.82	10.98	9.95	
Potential between metal and molal solution of ion, $M = M^{++} + 2e^-$ in volts	+ 1.70	+ 2.34	+ 2.87	+ 2.89	+ 2.90	
Heat of hydration of gaseous ions, kcal. approx.....		460	395	355	305	
Melting point $^{\circ}$ C.....	1300	650	851	757	850	(960)
Boiling point $^{\circ}$ C.....	(1500)	1107	1487	1384	1640	(1140)
Density of metal.....	1.73	1.75	1.55	2.6	3.75	6.0

**3. Chemical Properties.**—In all of their compounds the elements are present in the + 2 oxidation state, i.e. both of the two outer electrons are always lost when the elements enter into chemical reactions. It will be observed (Table I) that the oxidation potential of the heavier members of the group is as great as that of the alkali metals. Thus barium readily reacts with water, losing its electrons to the hydrogen of the water and forming barium ion and molecular hydrogen:  $Ba + 2H_2O = Ba^{++} + 2OH^- + H_2$ . The mechanism of the reaction involves taking the two electrons away from the barium and this, as given in Table I, requires about five volts for the first electron and ten for the second. These values of the ionization potentials are higher for the alkaline earth metals than for the alkali metals, and the reason that

barium is so readily oxidized to form the ion is to be found in the large heat of hydration of the barium ion. However, the rate of reaction of the second group elements with water is much slower than that of the alkali metals, even in the case of the more electropositive members; and magnesium and beryllium are scarcely attacked by water alone at ordinary temperatures. The metals burn brilliantly when heated in air or oxygen, forming the monoxide, except in the case of barium, which forms the peroxide. A certain amount of the nitride is also formed when burned in air, especially with magnesium, calcium, and radium. Because of their highly electropositive character the metals burn readily when ignited in carbon dioxide, forming the metal oxide and carbon. At low temperatures the metal surfaces are protected from rapid oxidation by oxide films; this is particularly true of beryllium and magnesium. Beryllium does not dissolve with appreciable speed in water even when boiled. Magnesium evolves hydrogen very slowly with cold water, while with calcium a slow stream of bubbles is observed. The metals all dissolve rapidly in acids. Beryllium dissolves in the alkali hydroxides in a manner similar to aluminum:  $\text{Be} + \text{OH}^- + \text{H}_2\text{O} = \text{HBeO}_2^- + \text{H}_2$ . Due to

TABLE II  
REACTIONS OF GROUP II METALS

$2\text{M} + \text{O}_2 = 2\text{MO}$	Ba also forms $\text{BaO}_2$
$\text{M} + 2\text{H}_2\text{O} = \text{M}(\text{OH})_2 + \text{H}_2$	Very slow with Be and Mg
$\text{M} + \text{H}_2 = \text{MH}_2$	With Ca, Sr, and Ba at high temperature
$\text{M} + 2\text{H}^+ = \text{M}^{++} + \text{H}_2$	
$4\text{M} + 10\text{H}^+ + \text{NO}_3^- = 4\text{M}^{++} + \text{NH}_4^+ + 3\text{H}_2\text{O}$	With dilute acid: $\text{H}_2$ also evolved
$\text{M} + \text{X}_2 = \text{MX}_2$	$\text{X}_2$ = any halogen
$3\text{M} + \text{N}_2 = \text{M}_3\text{N}_2$	High temperature
$3\text{M} + 2\text{NH}_3 = \text{M}_3\text{N}_2 + 3\text{H}_2$	Heated
$\text{M} + \text{S} = \text{MS}$	Also with Se and Te
$\text{M} + 2\text{C} = \text{MC}_2$	Especially with Ca, Sr.
	High temperature
$3\text{M} + 2\text{P} = \text{M}_3\text{P}_2$	Heated
$2\text{M} + \text{CO}_2 = 2\text{MO} + \text{C}$	Burn in $\text{CO}_2$

their action as strong reducing agents the metals are oxidized by many of the negative elements. A summary of the more important types of reactions is given in Table II.

**4. Occurrence.**—None of the elements of the group exists free in nature. The estimated percentages of the elements in igneous rocks are: calcium, 3.63; magnesium, 2.09; barium, 0.05; strontium,  $1.9 \times 10^{-4}$ ; beryllium,  $1 \times 10^{-5}$ ; and radium,  $10^{-12}$ . Beryllium compounds do not occur in large deposits but small quantities are found in many minerals and granitic rocks, usually as complex silicates and aluminates. The most important mineral is beryl,  $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ . Colored dark green with chromium it is known as emerald. A blue-green form is aquamarine. Masses of beryl weighing more than a ton have been found in New Hampshire. The elements are found in combination with practically all of the acid oxides. A few of the more important minerals are: magnesite,  $\text{MgCO}_3$ ; talc or soapstone,  $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ ; asbestos,  $\text{CaMg}_3(\text{SiO}_3)_4$ ; dolomite,  $\text{MgCO}_3 \cdot \text{CaCO}_3$ ; spinel,  $\text{Mg}(\text{AlO}_2)_2$ ; carnallite,  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ ; limestone,  $\text{CaCO}_3$ ; gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; fluor spar,  $\text{CaF}_2$ ; apatite,  $\text{Ca}_5(\text{PO}_4)_3\text{X}$ , ( $\text{X} = \text{Cl}$  or  $\text{F}$ ); strontianite,  $\text{SrCO}_3$ ; barites,  $\text{BaSO}_4$ . Magnesium and calcium chlorides and sulfates are present in sea water, the former in somewhat larger concentrations. Both elements are found as integral parts of animal and vegetable matter, although calcium is more prevalent than magnesium.

Radium is widely distributed in almost all rocks but in extremely small quantities. Primary uranium minerals contain about  $3.4 \times 10^{-7}$  grams of radium per gram of uranium (cf. XXII).

**5. Metals: Preparation and Uses.**—The metals are generally prepared by the electrolysis of their molten chlorides or fluorides to which alkali halides have been added to decrease the melting point. The common commercial electrolyte for magnesium is 70 per cent magnesium chloride and 30 per cent sodium chloride. The oxides or hydroxides can-



not be used because of their high melting points, although magnesium may be manufactured by the electrolysis of a molten solution of the oxide in fluoride similar to the process for aluminum (cf. VI—14). Calcium is prepared by the electrolysis of a mixture of the chloride and fluoride in a graphite crucible, which acts as the anode. The cathode is an iron rod just dipping into the molten salts. The liberated calcium adheres to the rod which is slowly raised, thus forming a long "stalk" of calcium. The metals are difficult to prepare by reduction with chemical agents; however, beryllium and magnesium chlorides may be reduced by sodium or potassium at high temperatures, and barium oxide is reduced by silicon at  $1,200^{\circ}$ . In a new commercial process for the manufacture of magnesium, a mixture of magnesium oxide and coal dust is heated to  $2,300^{\circ}$  C. in an electric furnace. At that temperature magnesium vapor may be distilled off.

Magnesium metal has considerable commercial importance. It is employed in signal flares and in photographic flash lights, usually in the form of powder; the latter use depends upon the high proportion of ultraviolet light in the flame formed by the combustion of the metal. It is also made into ribbon, the major part of which is now used in the degasification of radio tubes. Its importance in this connection is due to the absorption by the heated metal, not only of oxygen, but also of nitrogen through the formation of the nitride,  $Mg_3N_2$ . It is employed as a deoxidizer in casting bronze, nickel-silver, and monel metal. A small per cent of magnesium added to aluminum greatly increases the ease of machining of the latter. The composition of a number of magnesium alloys which are trade-marked, Dow-metal, A. M. Alloys, and Bohnalite X, is given in Table III.

Because of their low density (1.8) and high tensile strength these alloys are now widely used in the construction of airplanes, portable tools, and other machinery where light weight is important. The alloys are frequently treated

TABLE III  
COMPOSITION OF MAGNESIUM ALLOYS

	Use
Mg, 91.8; Al, 2.0; Mn, 0.2; Cd, 2.0; Cu, 4 . . . . .	Mold
Mg, 89.1; Al, 4.0; Zn, 0.4; Si, 0.5; Sn, 6.0 . . . . .	Wrought
Mg, 92; Al, 7.0; Zn, 0.75; Mn, 0.2 . . . . .	Sheet
Mg, 88.2; Zn, 4.5; Mn, 0.8; Si, 0.5; Sn, 6.0 . . . . .	Press forged
Mg, 9; Al, 91 . . . . .	Mold

with chromic or selenious acid solutions to give their surfaces a corrosion resistant film.

Calcium metal is used as a deoxidizer in the manufacture of many alloys and special steels. It is volatile at the temperature of molten steel and leaves no metallic residue. Some calcium silicide is used instead of the metal in certain steels. Although pure beryllium is brittle and has no industrial application, its alloys are rapidly becoming useful commodities. A 2.25 per cent beryllium alloy with copper is a remarkable spring material. A beryllium-cobalt-copper alloy combines high electrical conductivity with great hardness. Nickel with 1.8 per cent beryllium can be heat-treated to give values of tensile strengths as high as 260,000 pounds per sq. in. The addition of 0.5 per cent beryllium hardens gold and is said to increase the resistance of silver to tarnish. At present the high price of the metal prohibits its application in ferrous alloys.

Radium amalgam is formed upon the electrolysis of radium chloride solution using a mercury cathode. The mercury may be driven off by heating to leave the radium. The metal is said to blacken quickly due to the formation of the nitride.

## COMPOUNDS

**6. Oxides.**—The monoxides are difficultly fusible (Table IV) and extremely stable, remaining undecomposed at temperatures of 3,000° C. Their heats of hydration increase in order of the atomic weights.

TABLE IV  
OXIDES OF GROUP II

	BeO	MgO	CaO	SrO	BaO
Common name.....	beryllia	magnesia	lime	strontia	baryta
Melting point ° C.....	2,450	2,642	2,705	2,700	2,000
Heat of formation kcal. per mole.....	135.9	143.9	151.9	141.2	133.4
Heat of hydration $MO + H_2O = M(OH)_2$ ...		5.4	15.1	17.7	22.3
Solubility moles/liter of $M(OH)_2$ at 20° C.....	$5 \times 10^{-9}$	$3 \times 10^{-4}$	0.022	0.065	0.22
Decomposition temp. ° C. $M(OH)_2 = MO + H_2O$ (gas 1 at.).....			547	778	998

Beryllium oxide is as hard as corundum but the heavier oxides are soft. Beryllium oxide does not react with water. Magnesium oxide, if not ignited too strongly, reacts very slowly, while the rest of the group react rapidly. With lime the hydration reaction is called "slaking." The reaction starts slowly, but the heat evolved soon raises the temperature to a point where the reaction proceeds rapidly. The heat of slaking is sufficient, under some conditions, to cause the ignition of wood or other combustible material; hence the accidental slaking of stored lime often results in destructive fires.

The solid oxides crystallize in the sodium chloride type of ion lattice, with the exception of beryllium oxide, which is similar to zinc oxide (Append. V). The oxides are extremely poor conductors of heat.

The oxides of all except beryllium are generally prepared by the decomposition of the carbonates. The ease of decomposition decreases with increasing atomic weight, that is with increasing basicity of the metal oxide. The manufacture of lime is carried out in tall chimney-like furnaces known as lime kilns. The process is continuous; limestone is fed into the top, is heated and decomposed by a draft of hot gas, and the lime is removed at the bottom of the kiln.

The reaction is carried out at as low a temperature as possible to prevent the fusion of silicates present in the limestone which would render the lime inactive. In order to keep the temperature low the partial pressure of the carbon dioxide must also be kept low. In Fig. 1 are given the pressures of carbon dioxide in equilibrium with the oxide and carbonate at various temperatures. If calcium carbonate is heated in a retort under atmospheric pressure it requires a temperature of  $910^{\circ}\text{C}$ . to bring about decomposition; how-

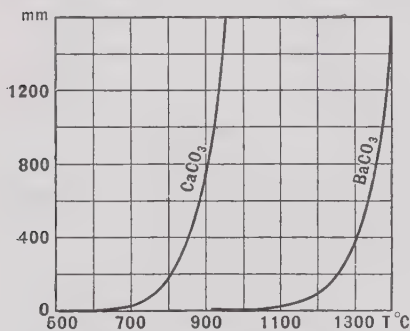


FIG. 1. Decomposition pressures of calcium and barium carbonates.

ever, in the operation of the lime kiln the blast of hot gases through the furnace keeps the partial pressure of the carbon dioxide at a low figure and permits the reaction to go to completion at temperatures much below  $910^{\circ}$ . In the case of barium carbonate, the decomposition temperature is so high that carbon is mixed

with the charge further to lower the partial pressure of the carbon dioxide:  $\text{C} + \text{CO}_2 = 2\text{CO}$ . Barium oxide is sometimes prepared from the nitrate, since it decomposes at much lower temperatures.

Magnesia in the form of bricks is used for lining furnaces and other refractory purposes. Mixed with asbestos it is employed as heat insulation for hot water and steam pipes. Other uses include: the manufacture of Sorel cement (Par. 9); absorbent in the manufacture of dynamite; vulcanization of rubber; adulterant of paint. Large quantities of mixed magnesium and calcium oxides are used for some purposes in place of pure magnesia, the mixture being produced by the calcination of dolomite.

The production of lime in the United States in 1937 was 4,000,000 tons. This was consumed chiefly (1) in making

the hydroxide (*vide infra*), used in plaster by the building industry, (2) in agriculture for soil treatment, and (3) in the chemical industries. Heated in the oxy-hydrogen flame, lime gives out an intense light, hence its former use in the "lime light." Calcium oxide is often employed as a dehydrating agent, for example, in the preparation of absolute alcohol and the drying of ammonia gas. A mixture of sodium hydroxide and calcium oxide, "soda-lime," is often employed to remove both water and carbon dioxide from gases. Lime containing more than 5 per cent magnesium oxide does not slake readily and is called "lean."

Barium oxide is the only one of the group which may be converted into the **peroxide**,  $\text{BaO}_2$ , upon heating in air, although with the exception of beryllium the peroxides may all be prepared by the action of hydrogen peroxide upon the metal ion. Barium peroxide is mentioned in connection with the preparation of oxygen and hydrogen peroxide. With water it readily forms the hydrate,  $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ .

**7. Hydroxides.**—The formation of the hydroxides from oxides has been discussed above. The alkaline reaction of the hydroxides is limited by their solubilities (Table IV); however, the hydroxides of calcium and the heavier members of the group may be classed as strong bases. Their salts with strong acids are very slightly hydrolyzed. Barium hydroxide is the only one which is stable enough to be heated to fusion.

**Beryllium hydroxide** is amphoteric (Hildebrand, *Prin. of Chem.*, p. 182), a fact which is not surprising in view of the very small size of  $\text{Be}^{++}$  (cf. III—7). The freshly precipitated hydroxide is said to have the formula  $\text{Be}_2\text{O}(\text{OH})_2$  and is metastable with respect to the form  $\text{Be}(\text{OH})_2$ . It dissolves in hydrogen ion to form  $\text{Be}^{++}$  but this ion hydrolyzes at low acid to form  $\text{Be}_2\text{O}^{++}$ .



The hydroxide is soluble in hydroxide ion to form  $\text{BeO}^{--}$  or  $\text{Be}_2\text{O}_3^{--}$  (beryllate or diberyllate).

Some **magnesium hydroxide** is prepared by the action of steam upon magnesium chloride:  $\text{MgCl}_2 + \text{H}_2\text{O} = \text{MgO} + 2\text{HCl}$ . The hydroxide is precipitated from a solution of magnesium ion upon the addition of a strong base. It belongs to the class of sparingly soluble bases which are soluble in excess of ammonium ion:  $\text{Mg}(\text{OH})_2 + 2\text{NH}_4^+ = \text{Mg}^{++} + 2\text{NH}_4\text{OH}$ .

Because of its low cost of production, **calcium hydroxide** is used commercially in many processes requiring hydroxide ion. A suspension of the solid in its saturated solution (milk of lime) is often employed. Among the more important uses are: the preparation of mortar, bleaching powder, ammonia, alkali hydroxide; purification of sugar and illuminating gas; removal of hair from hides; softening of water (Par. 11). The most extensive use is that in **mortar**. This is made by mixing slaked lime, one volume, with sand, three or four volumes, and water to make a thick paste. The mortar gradually hardens due, first, to the evaporation of water and the cementing action of the deposited hydroxide, and second, to the absorption of carbon dioxide from the air:  $\text{Ca}(\text{OH})_2 + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{O}$ . There follows a very slow formation of calcium silicate. The setting is accompanied by a decrease in volume but the presence of the large amount of sand prevents a large total shrinkage and renders the product porous.

**Strontium hydroxide** is made by heating the carbonate in steam:  $\text{SrCO}_3 + \text{H}_2\text{O} = \text{Sr}(\text{OH})_2 + \text{CO}_2$ . This reaction takes place at a lower temperature than the reaction:  $\text{SrCO}_3 = \text{SrO} + \text{CO}_2$ , due in part to the lowering of the partial pressure of the carbon dioxide by the steam, and in part to the energy of formation of the hydroxide from the oxide. The hydroxide crystallizes as  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . Strontium hydroxide is employed in the refinement of sugar to recover sugar from dilute solutions. Both calcium and



strontium ions form insoluble precipitates (saccharates) with sugar from hydroxide solutions, and these may be decomposed by the action of carbon dioxide. The strontium compound is somewhat the less soluble but the general practice in the sugar industry in the United States is to cool in solution and precipitate the calcium saccharate.

**Barium hydroxide** crystallizes with eight molecules of water. Its solution is known as "baryta-water," and is often employed as a standard alkali in quantitative analysis. The insolubility of the barium carbonate keeps the solution free from carbonate ion, which is usually present in sodium hydroxide and which is objectionable in titrating acids when certain indicators are used.

**8. Carbonates.**—Normal beryllium carbonate does not exist, but a basic carbonate is precipitated upon the addition of sodium carbonate to a soluble beryllium salt. The precipitate is soluble in excess of the reagent due to the formation of the beryllate ion,  $\text{Be}_2\text{O}_3^{--}$ .

Normal magnesium carbonate,  $\text{MgCO}_3$ , occurs in nature as the mineral, magnesite. A basic carbonate,  $\text{Mg}_4(\text{OH})_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ , is precipitated when an alkali carbonate is added to magnesium ion. The precipitate is soluble in excess ammonium ion due to the equilibria:  $\text{NH}_4^+ + \text{OH}^- = \text{NH}_4\text{OH}$ , and  $\text{NH}_4^+ + \text{CO}_3^{--} + \text{H}_2\text{O} = \text{HCO}_3^- + \text{NH}_4\text{OH}$ . The carbonate is also soluble in carbonic acid (see Calcium Carbonate below). The precipitated basic salt is used in medicine under the name "magnesia alba," partly as a mild alkali and partly for the physiological action of magnesium ion. Considerable quantities are consumed in the preparation of tooth powder and of silver polish. The natural carbonate and also the double carbonate with calcium, dolomite,  $\text{CaCO}_3 \cdot \text{MgCO}_3$ , are used for the commercial production of carbon dioxide. The compound  $\text{MgCO}_3(\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$  is precipitated upon the addition of ammonium carbonate to magnesium ion in a solution con-

taining 30 per cent alcohol. Advantage is taken of this fact in qualitative analysis.

Calcium carbonate crystallizes in two forms, calcite, rhombohedral, and aragonite, rhombic. The latter is unstable in respect to the former but the rate of transition is slow at ordinary temperatures. The heat of transition is about 300 cal. per mole. The carbonate is the most abundant of the calcium compounds. The most common forms are: Iceland spar, which is almost pure calcite; marble; limestone, which is less crystalline and contains clay and other silicates; chalk, which has been formed from the shells of minute marine organisms; shells and pearls.

The crystal structure of calcite is similar to that of sodium chloride, with the carbonate group replacing the chloride. The three oxygens are symmetrical about the carbon. Because of the size of the carbonate group the unit cube is distorted into a rhombohedron. Calcite is luminescent under the action of cathode rays. The glow persists for some time after the action of the rays has been stopped.

Calcium carbonate is precipitated upon the addition of carbonate ion. If the solution is boiling the precipitate is largely aragonite; in the cold it is finely divided calcite, which becomes coarse grained and distinctly crystalline upon standing. The solubility of calcium carbonate is increased in the presence of hydrogen ion due to the equilibrium,  $\text{H}^+ + \text{CO}_3^{--} = \text{HCO}_3^-$  (cf. XIII—10) and hence,  $\text{CaCO}_3 + \text{H}^+ = \text{Ca}^{++} + \text{HCO}_3^-$ . With excess acid, carbon dioxide is, of course, liberated. Due to the fact that the second ionization step of carbonic acid is much less than the first, calcium carbonate dissolves in carbonic acid:  $\text{CaCO}_3 + \text{H}_2\text{CO}_3 = \text{Ca}^{++} + 2\text{HCO}_3^-$ . This reaction occurs wherever water comes in contact with rock or soil containing calcium (or magnesium) carbonate, and imparts "hardness" to the water, which is objectionable for certain purposes (Par. 10). The bicarbonate solution upon heating loses carbon dioxide and the carbonate is again precipitated.

Stalactites and stalagmites are formed in caves by the precipitation of calcium carbonate brought about by the loss of carbon dioxide from water, which has been highly charged with the gas and thereby dissolved large quantities of limestone.

In addition to widespread use as building material, limestone is used in the manufacture of cement, lime, and glass. It is used in many metallurgical processes to form a flux with silica through the formation of calcium silicate.

Strontium and barium carbonates occur in nature as strontianite,  $\text{SrCO}_3$ , and witherite,  $\text{BaCO}_3$ , respectively. Next to the sulfates, they are the most important sources of these elements. The stability of the carbonates toward decomposition into the oxides increases, and the solubility in water decreases with increasing atomic weight. The general solubility equilibria of these carbonates with acid is similar to those of calcium, discussed above.

**9. Halides.**—The halides of beryllium, unlike most metallic halides, are very poor conductors of electricity in the fused state. The beryllium halides are highly hydrolyzed in solution, but not as much as the aluminum halides. The solutions upon evaporation yield basic salts.

The fluorides of the members of the group other than beryllium are insoluble in water, even in the presence of an excess of fluoride ion. The fluorides of calcium, strontium, and barium crystallize in ionic lattices of the so-called "calcium fluoride structure" (Append. V). Calcium fluoride occurs as the mineral fluorite or fluor-spar, and is important as the chief source of fluorine compounds. It is unusually transparent to ultraviolet light, nearly to  $0.1\ \mu$ .

The occurrence of magnesium chloride in salt deposits as double salts has been mentioned (cf. **IX—18**). It crystallizes from its water solution at room temperature as  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . This hydrate also occurs as the mineral, bischofite. The anhydrous salt cannot be prepared from the hydrate, as upon heating it loses hydrogen chloride:

$\text{MgCl}_2 + \text{H}_2\text{O} = \text{MgO} + 2\text{HCl}$ . This reaction may be employed for the manufacture of hydrochloric acid. Magnesium chloride combines with the oxide to form a basic chloride,  $\text{Mg}_2\text{OCl}_2$ . The heat of the reaction, 20 kcal., indicates that the compound is very stable. This reaction is the basis for the **Sorel cement** which is now used extensively as a substitute for tile. Magnesium chloride is often present in table salt, and its deliquescent nature frequently causes the salt to "cake" in damp weather. This may be avoided by the addition of enough sodium bicarbonate to form the basic magnesium carbonate.

A number of double compounds of calcium chloride occur as minerals, for example, tachydrite,  $\text{CaCl}_2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ , and apatite,  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$  (or  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ). The chloride may also be recovered from natural brines and salt deposits. Below  $30^\circ$  the salt crystallizes as the hexahydrate. Upon heating it may be dehydrated to form successively tetra-, di-, and monohydrates, and anhydrous salt. The latter contains some oxides formed through the loss of hydrogen

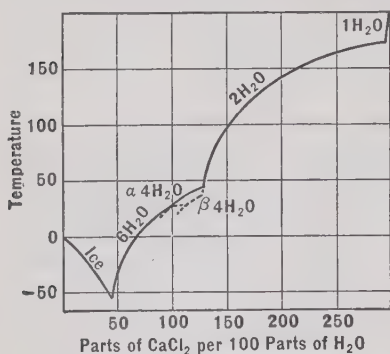


FIG. 2. The system calcium chloride and water.

chloride, as in the case of magnesium chloride discussed above. The solubility relations of the various hydrates are given in Fig. 2. The eutectic of the hexahydrate and ice is  $-55^\circ \text{C}$ . The anhydrous salt and dihydrate are used extensively as drying agents. The equilibrium pressure of water vapor for the reaction,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{O} = \text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ , is 0.92 mm. at  $0^\circ$ , and 3.78 mm. at  $20^\circ$ . Calcium chloride forms compounds with ammonia,  $\text{CaCl}_2 \cdot 8\text{NH}_3$ , and with alcohol,  $\text{CaCl}_2 \cdot 4\text{C}_2\text{H}_5\text{O}$ , and hence cannot be used for drying these substances; nor can it be used to dry hydrogen sulfide, which it de-

composes. Calcium chloride is used in the manufacture of calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , and in the manufacture of calcium carbide,  $\text{CaC}_2$ . It is also used in the manufacture of calcium cyanide,  $\text{CaCN}_2$ , and in the manufacture of calcium nitride,  $\text{Ca}_3\text{N}_2$ . It is also used in the manufacture of calcium phosphide,  $\text{Ca}_3\text{P}_2$ , and in the manufacture of calcium boride,  $\text{CaB}_2$ . It is also used in the manufacture of calcium silicide,  $\text{CaSi}_2$ , and in the manufacture of calcium sulfide,  $\text{CaS}$ . It is also used in the manufacture of calcium selenide,  $\text{CaSe}$ , and in the manufacture of calcium telluride,  $\text{CaTe}$ . It is also used in the manufacture of calcium fluoride,  $\text{CaF}_2$ , and in the manufacture of calcium chloride,  $\text{CaCl}_2$ .

composes somewhat with the evolution of hydrogen chloride.

The deliquescence of calcium chloride and its low cost make it useful in sprinkling roads. Its high solubility and the low freezing point of its solutions render it useful in refrigerating brines. Its principal commercial sources are ammonia recovery plants,  $2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 = 2\text{NH}_3 + \text{CaCl}_2 + 2\text{H}_2\text{O}$  (see Ammonia, **XII—6**) and the Solvay soda process (cf. **IV—13**), in both of which it results as a by-product.

Barium chloride is prepared for use as an analytical reagent by heating a mixture of barium sulfate, calcium chloride, and carbon:  $\text{BaSO}_4 + \text{CaCl}_2 + 4\text{C} = \text{BaCl}_2 + \text{CaS} + 4\text{CO}$ . The chloride is leached out and purified by recrystallization.

Radium is frequently prepared for commercial use in the form of chloride. Both the chloride and bromide are more insoluble than the corresponding barium compounds.

In general the solubilities of the alkaline earth halides increase in order of increasing atomic weight of the halogen, and decrease with increasing atomic weight of the metal.

**10. Sulfates.**—Beryllium sulfate is very soluble, and forms syrupy liquids from which it is difficult to crystallize a pure compound. The tetra- and hexahydrates have been obtained; the former is apparently unstable in respect to the latter.

Magnesium sulfate is found in many mineral waters and in the bittern of sea water. It occurs as the minerals kieserite,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ , and epsomite (epsom salts),  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . Between  $1.8^\circ$  and  $48^\circ$  the rhombic heptahydrate crystallizes from solution; below  $1.8^\circ$  a dodecahydrate separates; and at higher temperatures there are formed a number of lower hydrates. The anhydrous salt cannot be prepared, due to formation of basic sulfates upon heating the hydrates. Magnesium sulfate is used in weighting and sizing cotton, silk, paper, and leather; in fireproofing fabrics;



and in medicine as a purgative, and as a stimulant to increase the secretion of bile.

Calcium sulfate occurs in enormous deposits of **gypsum**,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (when pure white called alabaster); and less

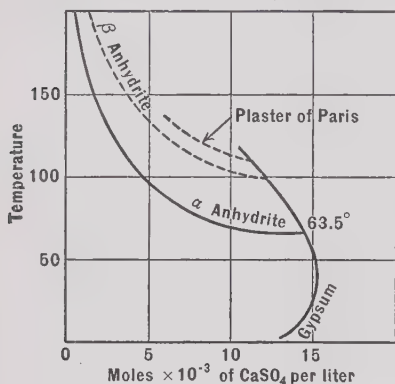


FIG. 3. The system calcium sulfate and water.

extensively as anhydrite, which is the anhydrous salt. The solid phase in equilibrium with the saturated solution is gypsum below  $63.5^\circ \text{C}.$ , and anhydrite above (Fig. 3). The solubility of the two salts at the transition point is 0.015 mole per liter. The solubility of anhydrite decreases rapidly with rising temperature and is only

0.002 mole per liter at  $150^\circ \text{C}.$  This decrease in solubility is partly responsible for the separation of boiler scale from water containing calcium sulfate (Hard Water, Par. 11). A second unstable and more soluble form of anhydrite also exists.

Upon heating, gypsum loses water to form the hemihydrate:  $2(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) = (\text{CaSO}_4)_2 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O}.$  The equilibrium pressure of water vapor reaches one atmosphere at  $107^\circ \text{C}.$  The hemihydrate is known as plaster of Paris. When it is mixed with water the equilibrium is reversed, and the plaster sets to a mass of gypsum crystals. The setting results in an increase in volume, and the plaster thus fills perfectly any mold into which it may be poured. In making plaster of Paris the gypsum must not be heated too strongly, as the anhydrous salt is then formed which absorbs water very slowly. Such plaster is called "dead burnt." The largest use of sulfate is in the manufacture of plaster for the interiors of buildings. Two varieties of plaster are made: (1) cement plaster, which is plaster of



Paris to which glue, glycerine, and other organic substances have been added as "retarders" to prolong the time of setting; and (2) hard finish plasters, such as Keenes cement, which is made by the calcination of the anhydrous sulfate with alum or borax. This second type of plasters sets very slowly, but gives a hard finish. Large quantities of sulfate are used in the manufacture of stucco and wall board and as a retarder for Portland cement (cf. **XIV—24**). The yearly consumption of gypsum in the United States is about six million tons.

There are two forms of the anhydrous calcium sulfate. One is comparatively unreactive to water but the other, sometimes called soluble anhydrite, absorbs water rapidly. The latter is marketed under the trade name of "Drierite" as a highly efficient desiccant for gases and liquids. Water remaining in air after drying with the reagent at 25° C. is said to be 0.005 mg. per liter.

Strontium sulfate,  $\text{SrSO}_4$ , celestite, and barium sulfate,  $\text{BaSO}_4$ , barite or heavy spar, are the most important minerals of these elements. These sulfates are extremely insoluble in water and dilute acids. They dissolve in concentrated sulfuric acid through the formation of  $\text{HSO}_4^-$ , and are reprecipitated upon dilution. When the sulfate is treated with sodium carbonate solution, some of the sulfate is converted into carbonate:  $\text{BaSO}_4 + \text{CO}_3^{--} = \text{BaCO}_3 + \text{SO}_4^{--}$ . At equilibrium the ratio of the molal concentration of sulfate to carbonate for the barium salts is about 0.01. If barium sulfate is treated, for example, with 100 cc. of  $\text{MNa}_2\text{CO}_3$ , 0.2 gram of barium carbonate will be formed. By decanting the solution and repeating the treatment, any amount of the sulfate may be converted into carbonate. The sulfate may also be converted into soluble salts by reduction with carbon at about 800° to form the sulfide, which may then be dissolved in acid. Barium sulfate is slowly dissolved by boiling with concentrated  $\text{HI}$ , because of reduction of the sulfate by iodide.

Barium sulfate is an important pigment. **Lithopone**, a mixture of barium sulfate and zinc sulfide, is prepared by the reaction:  $\text{BaS} + \text{ZnSO}_4 = \text{BaSO}_4 + \text{ZnS}$ . This pigment has excellent covering power and does not darken with hydrogen sulfide. Precipitated barium sulfate is also used as a pigment, especially as an adulterant of white lead, but its covering power is not good. Barium sulfate is further employed as a "filler" in wall paper and in glazed paper. It is taken internally in making X-ray photographs of the intestinal tract, on account of the opaqueness to X-rays of such a heavy atom as barium. The sulfate is the only barium salt which may be used, as it alone is sufficiently insoluble to prevent poisoning by the barium ion.

Radium sulfate is even more insoluble than barium sulfate. In the commercial extraction from uranium ores the sulfate is precipitated along with those of barium and lead, and converted into the chloride by either of the two methods discussed above.

**11. Water Softening.**—Water containing soluble calcium and magnesium salts is known as **hard water**. It is objectionable in the laundry because soap, which contains sodium or potassium salts of the higher fatty acids, such as stearic or palmitic acid ( $\text{C}_{17}\text{H}_{35}\text{COOH}$  and  $\text{C}_{15}\text{H}_{31}\text{COOH}$ ), forms insoluble salts with calcium and magnesium. This results in a waste of soap and the precipitate is a slimy curd which is difficult to remove. Hard water is objectionable in boilers because of the formation of boiler scale. The negative ions present in hard water are principally chloride, sulfate, and bicarbonate. Upon heating to a high temperature much of the dissolved material is precipitated as scale which is composed largely of anhydrite (Par. 10), calcium carbonate, and magnesium oxy-compounds. Such scale is a very poor conductor of heat, and its formation causes not only a waste of fuel, but also more rapid deterioration of the boiler through overheating at the surfaces where the heat is applied. Water which contains large quantities of

bicarbonate may be softened simply by heating:  $\text{Ca}^{++} + 2\text{HCO}_3^- = \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ . Such water is referred to as possessing **temporary hardness**. In many industrial plants water is softened by the addition of lime equivalent to the calcium bicarbonate present, and sodium carbonate equivalent to the additional calcium and magnesium:  $2\text{HCO}_3^- + 2\text{OH}^- + 2\text{Ca}^{++} = 2\text{CaCO}_3 + 2\text{H}_2\text{O}$ , and  $\text{Ca}^{++} + \text{CO}_3^{--} = \text{CaCO}_3$ .

In the **zeolite** or "**permutite**" process water is softened by filtering slowly through artificial or natural zeolite, which is a hydrated sodium aluminum silicate. Although the composition varies somewhat in the different forms,  $\text{NaH}_6\text{AlSiO}_7$  may be written as an approximate formula. The sodium is replaceable by calcium, magnesium, ferrous, and other  $+2$  ions.  $2\text{NaH}_6\text{AlSiO}_7 + \text{Ca}^{++} = \text{Ca}(\text{H}_6\text{AlSiO}_7)_2 + 2\text{Na}^+$ . The equilibrium is reversible and when the efficiency of the zeolite drops, it may be regenerated by treating for a few hours with a concentrated solution of sodium chloride. The process is inexpensive as only sodium chloride is consumed.

A considerable quantity of ferrous iron is frequently present in surface water. This is especially objectionable in the laundry because of the yellow color imparted to the cloth by the oxidation of the iron to the ferric state. The iron is removed by either the lime-carbonate, or the zeolite processes, or by spraying the water to give intimate contact with the air, which oxidizes the iron to insoluble ferric hydroxide.

The use of tetrasodium pyrophosphate,  $\text{Na}_4\text{P}_2\text{O}_7$ , and hexasodium hexaphosphate,  $\text{Na}_6\text{P}_6\text{O}_{18}$ , is increasing in washing technology. These salts hold the calcium in solution as complex ions, e.g.,  $\text{Ca}_2\text{P}_6\text{O}_{18}^{--}$ , and thus prevent the formation of curds. Since it is the fatty acids, containing the  $-\text{COOH}$  group which tend to precipitate the calcium in ordinary soap, a number of new detergents have been introduced which do not have this acid radical. The

sodium salt of the sulfuric ester of cetyl alcohol,  $C_{16}H_{33}OSO_3Na$  and cetyl trimethyl ammonium bromide,  $C_{16}H_{33}(CH_3)_3NBr$ , are examples.

**12. Carbides.**—At a very high temperature the metals or their oxides react with carbon forming carbides. The most important is calcium carbide,  $CaC_2$ , which is produced on a large scale by heating a mixture of lime and carbon to a temperature of about  $3,000^\circ C$ . in an electric furnace:  $CaO + 3C = CaC_2 + CO$ . Calcium carbide reacts with water to form acetylene (cf. **XIII—18**):  $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$ . It may, therefore, be called calcium acetylide. Another important reaction of the carbide is the absorption of nitrogen at about  $1,000^\circ C$ . to form cyanamide:  $CaC_2 + N_2 = CaCN_2 + C$ . This reaction is the basis for the cyanamide process for the fixation of nitrogen (cf. **XII—8**).

**13. Hydrides.**—Beryllium and magnesium do not readily form hydrides; but calcium, strontium, and barium react readily with hydrogen at high temperature (about  $600^\circ$ ). The large heats of the reactions, e.g.,  $CaH_2$ , 46 kcal., indicate the stable nature of these hydrides. Like the alkali hydrides, the hydrogen possesses a negative charge and is liberated at the anode upon electrolysis of the molten salts. Calcium hydride, although expensive, is an easily portable source of hydrogen for war balloons. One mole reacts with water to give two moles of hydrogen:  $CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$ .

**14. Nitrates.**—Calcium nitrate is a constituent of fertile soils. The salt is produced for use as fertilizer by the electric arc process for the fixation of nitrogen (cf. **XII—32**). It crystallizes as  $Ca(NO_3)_2 \cdot 4H_2O$  at ordinary temperatures and is very soluble. Strontium nitrate is used in the manufacture of red fire. Barium nitrate is the least soluble of the group, and is precipitated as the anhydrous salt upon the addition of barium ion to solutions containing high concentrations of nitrate. It is sometimes used in making green fire.

**15. Sulfides.**—The sulfides may be formed by the direct union of the elements, or by reduction of the sulfates by carbon. The compounds so prepared dissolve but slowly in water, but the apparent insolubility is merely a matter of rate of solution. Solutions of these sulfides, like those of all soluble sulfides, are highly alkaline due to hydrolysis of the sulfide ion. Calcium sulfide is used as a depilatory. The use of barium sulfide has been mentioned in the preparation of lithopone. Both of these sulfides glow in the dark after exposure to sunlight, and are used in the preparation of luminous paint. This property is apparently due to the presence of traces of impurities, especially vanadium and bismuth. In the regions about the particles of impurities, the crystal is able to absorb radiant energy through the displacement of electrons to higher energy levels. The rate at which the electrons return to the stabler positions is slow, so that the absorbed energy is re-emitted over a period of time.

**16. Phosphates.**—The calcium phosphates are the most important of the group. They occur as the tri- and di-calcium orthophosphate,  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{CaHPO}_4$ ; and as fluor and chlor apatites (Par. 4). Dried bones consist largely of calcium phosphate. Millions of tons of the insoluble tricalcium salts are treated yearly with sulfuric acid to convert into soluble acid phosphate,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , for use as fertilizer (see Superphosphate, **XI—54**). Ammonium magnesium phosphate,  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ , is important in analytical work (Par. 18).

**17. Other Important Compounds.**—A number of compounds containing the alkaline earths are discussed under other headings: bleaching powder (cf. **X—13**), glass (cf. **XIV—23**), cement (cf. **XIV—24**), asbestos (cf. **XIV—20**), talc (cf. **XIV—21**).

**18. Analytical Properties of Alkaline Earth Ions.**—The chemistry of the alkaline earth ions is comparatively simple, as they form no complexes with other ions (a few



exceptions with beryllium), and few insoluble compounds. The ions are colorless. Beryllium ion has a sweet taste, magnesium ion a bitter taste, and calcium ion is practically tasteless. Barium ion is extremely poisonous. The solubilities of the various hydroxides has been discussed (Par. 7). The solubilities of the chromate and sulfate decrease with increasing atomic weight; and likewise the carbonate, with the exception that strontium carbonate is more insoluble than barium. The group, not including beryllium, is separated from all other positive ions except the alkalies by taking advantage of the fact that they are not precipitated by a solution of ammonium sulfide. Ammonium carbonate precipitates  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{BaCO}_3$ ; and if about 30 per cent alcohol is present,  $\text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3$ . Radium is separated from barium by fractional crystallization of the chlorides, bromides, or chromates, the compounds of the latter being the more soluble. Barium may be separated from the lighter members of the group by the greater insolubility of the chromate. Strontium is separated from calcium in solution by the addition of a dilute solution of sulfate, which precipitates strontium sulfate but not calcium. Magnesium is separated from the heavier elements of the group through the solubility of the carbonate in ammonium salts. The insoluble nature of beryllium hydroxide permits its ready separation from the remainder of the group. It may be distinguished from aluminum by the solubility of the beryllium hydroxide in excess bicarbonate, probably due to the formation of a complex bicarbonate ion.

Calcium may be precipitated quantitatively as calcium oxalate by the addition of ammonium oxalate. The precipitate is composed of larger crystals, and is more easily filtered if precipitated from a slightly acid solution, in which it is somewhat soluble. The final traces of calcium may then be removed by making the solution alkaline with ammonium hydroxide. The oxalate may be dried and



weighed as such or ignited to form the carbonate:  $\text{CaC}_2\text{O}_4 = \text{CaCO}_3 + \text{CO}$ .

Barium is usually precipitated and weighed as sulfate (cf. **XI—33**); while strontium may be determined as sulfate or oxalate. Magnesium ammonium phosphate,  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ , is precipitated upon the addition of sodium phosphate and ammonium hydroxide to a solution of a magnesium salt. Upon ignition the pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7$ , is formed, and may be weighed as such:  $2\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O} = \text{Mg}_2\text{P}_2\text{O}_7 + 2\text{NH}_3 + 13\text{H}_2\text{O}$ .

The sodium rhodizonate spot test is a convenient method of distinguishing between calcium, barium, and strontium. One drop of an 0.4 per cent solution of the reagent is placed on a filter paper. One drop of test solution is placed on the drop and then one drop of ethyl alcohol. Barium and strontium give red coloration. If the spot is now touched with one drop of 0.3*N* HCl, barium will remain bright red but strontium will dissolve.

**19. Spectra.**—Beryllium and magnesium compounds do not ionize sufficiently to impart color to the Bunsen flame. Volatile calcium compounds give a brick red, strontium a carmine, barium a yellow green, and radium a crimson flame. The coloration is very intense with the chlorides, but is not satisfactory with the oxides or sulfates due to their low volatility. The electric arc spectra afford a much more delicate means of determining the presence of the alkaline earth elements, 0.002 mg. of calcium being detectable. The material to be analyzed is usually placed upon the positive pole of the arc. The wave lengths in  $\mu\mu$  ( $10^{-6}$  mm.) of the more prominent lines are: calcium 423, 616; strontium 422, 461; barium 455, 493; magnesium 516.8 to 518.4, a group of three lines.

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# Chapter VI

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## GROUP III. BORON, ALUMINUM

1. The third periodic group, like the first and second groups, is divided into a main group with kernels of the noble gas type, and a subgroup with kernels of the eighteen electron type. The elements of the main group are boron, aluminum, scandium, yttrium, lanthanum (and Rare Earths), and actinium; those of the subgroup are gallium, indium, and thallium. Although the Rare Earths may be considered as members of the third main group, they constitute a family which is so unique from the standpoint of atomic structure that it seems advisable to discuss them in a separate chapter (cf. **XXI**). Due to the great similarity of scandium, yttrium, and lanthanum to the Rare Earths, the detailed consideration of these three elements will be postponed to that chapter. Actinium is of interest chiefly on account of its radioactivity, and will, therefore, be taken up in that connection (cf. **XXII**). The subgroup elements are discussed in Chapter **IX**.

Boron is a nonmetal, but the remainder of the group are highly metallic. The melting points of the group are fairly high (Table I), and exhibit no regular trend from the light to the heavy elements. An oxidation state of +3 is shown by these elements in all of their compounds with the exception of a few relatively unstable compounds of boron. The oxides or hydroxides are less basic than those of the alkaline earth elements, as is to be expected from the increased charge on the positive ions. Boron oxide

is distinctly acidic and shows only faint basic properties. Aluminum oxide is amphoteric, while scandium, yttrium, and lanthanum show no acid properties and are distinctly, though not strongly, basic. This increase in basic character of the oxides within the group is again to be correlated with the increasing size of the ions of the heavier members (cf. III—7).

The elements are somewhat less electropositive than the alkaline earth metals. The energies required to ionize the electrons from the gaseous atoms are very high, as shown for aluminum in Table I; hence the high values for the electrode potentials of the elements must be due to even greater energies of hydration of the positive ions. In the case of aluminum this is over a thousand kilogram-calories.

TABLE I  
ATOMIC AND PHYSICAL PROPERTIES

	B	Al		B	Al
Atomic weight . . .	10.82	26.97	Ionization		
Atomic number . . .	5	13	potentials in		
Isotopes . . . . .	10, 11	none	volts, 1st. . . . .	8.26	5.96
Electrons in various			2d . . . . .	25.00	18.74
quantum levels,			3d . . . . .	37.75	28.31
1st. . . . .	2	2	Electrode		
2d . . . . .	3	8	potential		
3d . . . . .		3	$M = M^{+++} +$		
Melting points °C.	2,300	658	$3e^-$ , volts 25°		1.67
Boiling points °C. .	2,550	1,800	Electral resistivity		
Density . . . . .	2.4	2.70	20° C. ohm-cm.	$1.8 \times 10^6$	$2.62 \times 10^{-6}$
			Radius of $M^{+++}$		
			in crystals,		
			cm. $\times 10^8$	0.20	0.50

## BORON

**2. Occurrence.**—Boron constitutes but a small portion of the earth's crust, estimated as about 0.001 per cent. It occurs as boric acid,  $H_3BO_3$ , and as borates. The principal deposits have resulted from the evaporation of inland seas. In the Stassfurt area in Germany the deposits are chiefly

magnesium borates; while in the arid regions of western United States they consist largely of colemanite,  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ , with some borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ . Recently large deposits of kernite,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ , have been discovered in Kern County, California. Boron is widely distributed in rocks in complex silicates and aluminates, such as tourmaline,  $\text{H}_2\text{MgNa}_3\text{Al}_3(\text{BO})_2\text{Si}_4\text{O}_{20}$ .

**3. Preparation and Properties.**—No satisfactory electrolytic method has been developed for the production of boron. It is usually prepared by the reduction of the oxide by powdered magnesium:  $\text{B}_2\text{O}_3 + 3\text{Mg} = 3\text{MgO} + 2\text{B}$ ; but other powerful reducing agents, such as sodium, may be used and the halides may be substituted for the oxide. The product of the reduction is amorphous boron, and, when magnesium is used, it is mixed with magnesium boride,  $\text{Mg}_3\text{B}_2$ , the proportion of which may be minimized by using excess of boric oxide, but in this case some suboxide, possibly  $\text{B}_3\text{O}$  remains. If this product is heated in an electric furnace with an atmosphere of hydrogen a crystalline boron is obtained. When the reduction was first carried out with aluminum the product was thought to be crystalline boron, but further investigation has indicated that it consists of a mixture of aluminum borides, such as  $\text{AlB}_{12}$ .

Small crystals of boron have been prepared by the reduction of the trichloride with hydrogen when heated by a tungsten filament to a temperature around  $1,500^\circ \text{C}$ .

The free element, as usually prepared, is a dark brown powder. The cooled fused material is brittle, almost as hard as diamond, and practically a non-conductor of electricity.

**4. Reactions.**—Boron oxidizes slowly in air at  $100^\circ \text{C}$ ., and burns at higher temperatures with a green flame. It ignites in fluorine at room temperature, and in the other halogens at higher temperatures. From the potential  $+0.73$  volt for the half reaction,



the element should dissolve readily in acid. However no reaction occurs, the slowness doubtless being due to the large initial energy required to break the strong bonds in the solid. It does dissolve in fused alkalis due to the stability of the borates. It is readily oxidized by strong oxidizing agents, such as nitric acid, concentrated sulfuric acid, and ferric ion. It does not combine directly with hydrogen. These and other reactions are summarized below.

TABLE II  
REACTIONS OF BORON

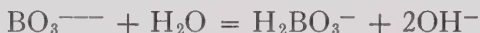
$4B + 3O_2 = 2B_2O_3$	Burns with green flame
$2B + 3X_2 = 2BX_3$	With halogens
$2B + 3S = B_2S_3$	At about $600^\circ$
$2B + N_2 = 2BN$	Above $1,200^\circ$
$2B + 2NH_3 = 2BN + 3H_2$	Heated
$2B + 6KOH = 2K_3BO_3 + 3H_2$	Fused with alkali
$B + HNO_3 + H_2O = H_3BO_3 + NO$	
$nB + mM = M_mB_n$	With a large number of metals

**5. Oxides.**—Boron forms the oxide  $B_2O_3$ , and there is evidence of suboxides  $BO$  or  $B_3O$ . The sesquioxide may be prepared by heating boric acid to red heat. The product is a very hard, brittle glass. The oxide dissolves most metal oxides to form clear glasses. The sesquioxide takes up water rather rapidly to form the acid, and since it is otherwise very non-reactive, it often serves as a convenient dehydrating agent.

**6. Boric Acid and Borates.**—The addition of strong acids to borates liberates the weak boric acid, and this crystallizes from the water solution as the ortho-acid,  $H_3BO_3$ . The solubility increases markedly with temperature; a saturated solution contains 2.6 per cent at  $0^\circ$ , and 28.7 per cent at  $100^\circ C$ . The acid is somewhat volatile from hot solutions, possibly due to the formation of volatile hydrates. Upon heating, the ortho-acid loses water to form first the meta-acid,  $HBO_2$ , and then the tetraboric acid,  $H_2B_4O_7$ . In water solution the ortho-acid acts as a weak monobasic

acid i.e., its reactions are those of the meta-acid,  $\text{HBO}_2$ . The dissociation constant as calculated for the reaction,  $\text{H}_3\text{BO}_3 = \text{H}^+ + \text{H}_2\text{BO}_3^-$ , is  $5.8 \times 10^{-10}$ . The equilibrium is complicated, above concentration of  $0.5M$  by the formation of  $\text{HB}_4\text{O}_7^-$ . The acid is used in medicine, under the name "boracic acid," as a mild antiseptic.

Very few orthoborates are known, and in water solution they hydrolyze:



Upon the addition of hydroxide to the ortho-acid the equilibrium,  $2\text{BO}_2^- + 2\text{HBO}_2 = \text{H}_2\text{O} + \text{B}_4\text{O}_7^{--}$ , is established, the equilibrium constant being about  $10^3$ . The constants for the first and second ionization of  $\text{H}_2\text{B}_4\text{O}_7$  appear to be about  $10^{-4}$  and  $10^{-9}$ , respectively. Many of the metaborates are but moderately soluble, e.g.,  $\text{AgBO}_2$ ,  $\text{Ba}(\text{BO}_2)_2$ ,  $\text{Pb}(\text{BO}_2)_2$ . With sodium hydroxide the salt,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , **borax**, forms, and may be crystallized from the solution below  $60^\circ \text{C}$ . Above that temperature a pentahydrate is stable. The naturally occurring kernite, which is the tetrahydrate, is a metastable form and has not been prepared in the laboratory.

Borax is the most important compound of the element. It is but sparingly soluble at  $0^\circ \text{C}$ ., 1.3 g. per liter, but is very soluble at the temperature of transition to the pentahydrate. The solution is slightly alkaline by hydrolysis,  $0.1N$  solution containing about  $2 \times 10^{-5}N \text{OH}^-$ . Borax is prepared from naturally occurring borates by (1) the extraction of the acid, and (2) the reaction of the acid with sodium carbonate:  $4\text{H}_3\text{BO}_3 + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{B}_4\text{O}_7 + 6\text{H}_2\text{O} + \text{CO}_2$ .

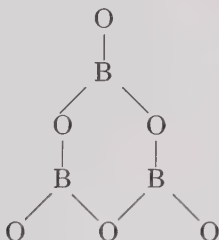
Borax fuses to form a glass which is capable of dissolving metal oxides, since it contains an excess of acid oxide, e.g.  $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 + \text{CuO} = \text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 + \text{CuO} \cdot \text{B}_2\text{O}_3$ . Upon this property depends its use in soldering and welding to clean the metal surface of coatings of oxides. Many oxides dissolved in fused borax impart characteristic colors,



the familiar borax bead tests (Append. VII). The colored glass finds use as artificial gems, and when ground, as pigments. Among other important uses of borax are the manufacture of glass, enamels, and soap, sizing for paper, and as a preservative for wood and meats.

Besides the borates above mentioned there exist a very large number of polyborates, salts of the acids,  $(B_2O_3)_n \cdot (H_2O)_m$ , where  $n$  may be as large as six and  $m$  is usually one, two, or three.

In boric acid the  $BO_3$  group is planar with the oxygens forming a triangle about the boron. In calcium metaborate the  $BO_2$  groups form chains of triangles linked together by holding oxygen atoms in common, and in potassium metaborate,  $K_3B_3O_6$ , the structure of the negative ion is,



7. Boric acid forms with methyl alcohol the rather volatile methyl borate,  $(CH_3)_3BO_3$ . This compound burns with a green flame. The corresponding ethyl borate is less volatile. The very slightly basic nature of boric acid is shown by the reaction between boiling boric acid and phosphoric acid to give **boron phosphate**,  $H_3BO_3 + H_3PO_4 = BPO_4 + 3H_2O$ . Borax fused with ammonium chloride forms boron nitride:  $Na_2B_4O_6 + 4NH_4Cl = 4BN + 2NaCl + 7H_2O + 2HCl$ . **Boryl sulfate**,  $(BO_2)_2SO_4$ , is formed by the action of sulfur trioxide upon boron trichloride.

8. **Peroxyborates.**—Peroxyborates may be prepared by the action of peroxides upon borates or by the electrolytic oxidation of borate solutions. The most important of these compounds is the sodium salt,  $NaBO_3 \cdot 4H_2O$ . It is used as

a bleaching agent, and as an antiseptic constituent of certain tooth powders.

**9. Borides.**—In addition to the borides of magnesium and aluminum mentioned above, a large number of borides have been prepared, among which the following may be mentioned:  $\text{AlB}_2$ ,  $\text{CaB}_6$ ,  $\text{BaB}_6$ ,  $\text{CB}_4$ ,  $\text{SiB}_6$ ,  $\text{ThB}_4$ ,  $\text{CrB}$ ,  $\text{WB}_2$ ,  $\text{FeB}$ ,  $\text{Fe}_2\text{B}$ ,  $\text{NiB}$ ,  $\text{CoB}$ .

The so-called boron carbide,  $\text{CB}_4$ , may be made by the reduction of boric acid with carbon in the electric arc furnace. In spite of its great hardness, it may be cast and molded.

**10. Halides.**—The halides are gases, or easily volatile liquids. The melting and boiling points parallel the corresponding values for the halogens.

	$\text{BF}_3$	$\text{BCl}_3$	$\text{BBr}_3$	$\text{BI}_3$
Boiling point.....	− 101.9	13	90.5	210
Melting point.....	− 128	− 107	− 44	43

They may be prepared by the direct union of the elements, but are usually formed from boric oxide, using hydrogen fluoride in the case of fluorine,  $\text{B}_2\text{O}_3 + 6\text{HF} = 2\text{BF}_3 + 3\text{H}_2\text{O}$ ; and in the case of the other halogens using the halogen and carbon at elevated temperatures:  $\text{B}_2\text{O}_3 + 3\text{C} + 3\text{X}_2 = 2\text{BX}_3 + 3\text{CO}$ . The fluoride is used commercially as a catalyst, one of the more important reactions being the reaction of an alcohol and carbon dioxide at high temperatures to form an organic acid. The three heavier halides are completely hydrolyzed in water:  $\text{BX}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{BO}_3 + 3\text{H}^+ + 3\text{X}^-$ . The fluoride reacts with water to form boric acid and fluoboric acid:  $4\text{BF}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{BO}_3 + 3\text{HBF}_4$ . Pure fluoboric acid is unstable, but many of its salts are known. Boron fluoride also forms a complex with ammonia,  $\text{BNH}_3\text{F}_3$ . The probable electronic formulae of the fluoride, the ammonia complex, and fluoboric acid are, respectively:



**11. Hydroborons.**—There are a number of compounds of hydrogen and boron which resemble the hydrocarbons in their non-polar nature. They are often referred to as the boron hydrides, but it seems advisable to restrict the use of the term “hydrides” to compounds in which the hydrogen is definitely negative. The addition of magnesium boride to 4*N* HCl at about 45° results in the evolution of a gas which is mainly hydrogen, but contains as well the compound, B<sub>4</sub>H<sub>10</sub>, borobutane, and small amounts of B<sub>5</sub>H<sub>9</sub>, B<sub>6</sub>H<sub>10</sub>, and B<sub>6</sub>H<sub>12</sub>. Borobutane boils at 10° and melts at −112°. It has a disagreeable odor, is toxic, and ignites spontaneously when exposed to air. The gas is unstable in respect to decomposition into B<sub>2</sub>H<sub>6</sub> and a number of complex solids and liquids. The compound, BH<sub>3</sub>, does not appear to be stable, possibly due to polymerization. The structure of these compounds is difficult to explain, as there are not enough electrons in B<sub>4</sub>H<sub>10</sub>, for example, to account for all the necessary bonds if each has an electron pair. The assumption has been made, that in these compounds we have examples of one electron bonds.

**12. Analytical.**—The green flame test of methyl borate is often employed as a qualitative test. The sample is placed in a test tube, and sulfuric acid and methyl alcohol

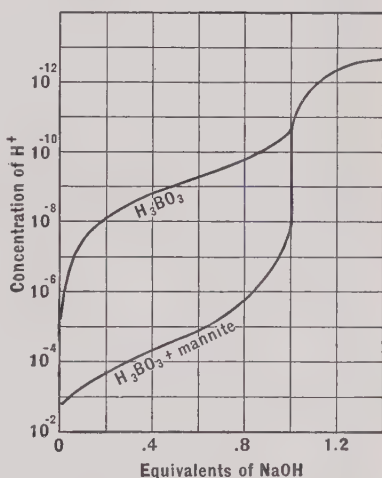


FIG. 1. Titration curves for boric acid.

added. The vapors which escape upon gentle warming burn with a green flame when ignited.

Methyl orange does not react acid to boric acid, therefore soluble borates may be titrated with that indicator. Pure boric acid is difficult to titrate with a strong base, as the equivalent point is highly alkaline as indicated in Fig. 1. The addition of glycerol, mannite, or other polyalcohols which form complex ions with  $\text{BO}_2^-$ , has the effect of increasing the strength of the acid, and bringing the equivalent point into the range of phenolphthalein; hence the acid may be titrated using that indicator.

## ALUMINUM

**13. Occurrence.**—Aluminum ranks third among the elements in order of abundance. The estimated abundance in per cent in the igneous rocks is 8.13. It is the most abundant of the metallic elements. The most common minerals are the aluminosilicates, which include the feldspars, as  $\text{KAlSi}_3\text{O}_8$ ; the micas, as  $\text{H}_2\text{KAl}_3(\text{SiO}_4)_3$ ; and clays (kaolin), as  $\text{H}_2\text{Al}_2(\text{SiO}_4)_2\text{H}_2\text{O}$ . Cryolite,  $\text{Na}_3\text{AlF}_6$ , and bauxite,  $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ , are important in the production of the metal. Ruby, sapphire, and corundum are forms of the oxide. Garnet is, approximately,  $[\text{Ca}, \text{Mg}, \text{Fe}]_3[\text{Al}, \text{Fe}]_2(\text{SiO}_4)_3$ ; and turquoise,  $\text{Al}_2(\text{OH})_3\text{PO}_4 \cdot \text{H}_2\text{O}$ , colored by copper phosphate.

**14. Preparation.**—The metal was first prepared commercially about 1850 by the reduction of the chloride by sodium at high temperature. Shortly thereafter methods were developed for the electrolysis of mixtures of molten aluminum, sodium fluorides, and chlorides, but the metal remained rare and expensive until the simultaneous discovery by Hall and by Héroult of the electrolysis of the oxide in molten cryolite in 1886, which laid the foundation of the modern aluminum industry. In the Hall process, the electrolysis is carried out in large iron pots with a thick

carbon lining which acts as the cathode. A number of large graphite rods sticking down into the pot serve as the anode. The graphite rods are first lowered until they touch the cathode and an arc is struck; powdered cryolite is then added and melted by the heat of the arc. When a sufficient liquid bath is obtained, aluminum oxide is added and the anodes drawn farther away from the cathode. The addition of the oxide raises somewhat the resistance of the liquid. The temperature of the bath is kept at about  $1,000^{\circ}\text{C.}$ , and since this is above the melting point of the metal, it collects as a liquid in the bottom of the cell and is drawn off at intervals. Oxygen is liberated at the anode and gradually burns away the graphite. The cell reaction is:  $2\text{Al}_2\text{O}_3 = 4\text{Al} + 3\text{O}_2$ . Ordinary commercial aluminum is about 99.0 to 99.5 per cent pure. It is very difficult to refine the impure metal, so the oxide is carefully purified before electrolysis (see Oxide). Recently, however, aluminum of 99.85 per cent purity has been made electrolytically from an alloy of aluminum, copper, and silicon. The cell consists of three liquid layers of decreasing density; the lowest is the alloy, which is made the anode; the middle layer consists of molten salts; and the top layer is pure aluminum, which is made the cathode. Aluminum may be electroplated from a bath containing aluminum chloride and bromide dissolved in ethyl bromide and benzene.

**15. Properties.**—The metal is extremely light, density 2.7, and possesses high tensile strength. Although its specific electrical conductivity is less than copper, weight for weight it is twice as good a conductor. It is easily malleable and may be rolled into thin foil. It has a silvery appearance when freshly cut, but the ordinary surface has a dull white luster, since it is covered by a thin, firm coat of oxide which protects the surface from further oxidation.

**16. Uses.**—In addition to the common use in household utensils, the metal is becoming increasingly important in

the construction of airplanes and other machines where light weight is essential. Two important uses are as foil in place of tin foil, and as a "silver" paint. The latter is made by mixing the thin metal flakes with oil. Aluminum wire to the extent of 500,000 miles was in use in the United States in 1937, chiefly in transmission lines. The metal is used to remove dissolved oxygen in casting iron and steel, and thus to prevent blow holes. It is also used in "thermite" (Par. 17). The metal can be welded, but it is soldered with difficulty. Many of the alloys are important, especially those with Cu, Si, Mn, Mg, Fe, and Zn. The pure metal is difficult to work on the lathe as it sticks to the tools, but many of the alloys may be machined readily. "**Duralumin**" contains 4 per cent copper, 0.8 per cent magnesium, and 0.6 per cent manganese; and when hardened by quenching, possesses a tensile strength of 60,000 lb. per sq. in., as compared to 30,000 lb. for the pure metal. **Magnalium** has the composition, aluminum 90–95 per cent and magnesium 5–10 per cent. See also magnesium and copper.

**17. Reactions.**—Aluminum is a very base metal, but its surface is protected so thoroughly by its oxide coating that it may be melted in air without serious oxidation. However, at high temperatures the metal burns vigorously, and aluminum powder and liquid oxygen unite with a flash if ignited with a match. The metal does not dissolve in water unless the surface is amalgamated. The oxide does not adhere to the amalgamated surface, and the metal is free to show its true electropositive nature by reacting with water or by oxidizing rapidly in air. The metal dissolves readily in hydrochloric acid, and slowly in sulfuric acid, but is rendered passive by nitric acid so that this acid is often shipped in aluminum containers. It dissolves rapidly in nitric acid, however, if a small amount of mercuric salt is present. Nitric oxide is evolved from concentrated acid, and ammonium nitrate formed with



dilute. Concentrated alkalis dissolve the metal with the evolution of hydrogen and the formation of the aluminate. The granulated metal reduces many oxides and sulfides upon ignition, the so-called "**Goldschmidt reaction.**" A mixture of aluminum and iron oxide, known as "**thermite,**" is used in welding. The heat of the reaction is such that a temperature of about  $3,000^{\circ}$  is produced, and the iron formed by the reduction can be run as a white hot liquid into the crack to be welded. To start the termite reaction an ignition powder is required, such as a mixture of barium peroxide and aluminum.

The aluminum electrode is highly irreversible, and extremely difficult to measure directly. The value, 1.67 volts, is calculated from thermal data and indicates that aluminum is about as electropositive as magnesium.

The irreversibility of the aluminum electrode is made use of in rectifying alternating currents. When acting as anode, the electrode has enormous resistance, but as cathode it has low resistance; hence cells with an aluminum electrode allow one half of an alternating current to pass but not the other. The cell is most effective with a phosphate electrolyte.

TABLE III  
REACTIONS OF ALUMINUM

$2\text{Al} + 3\text{O}_2 = \text{Al}_2\text{O}_3$	
$2\text{Al} + 6\text{H}^+ = 2\text{Al}^{+++} + 3\text{H}_2$	
$2\text{Al} + 2\text{OH}^- + 4\text{H}_2\text{O} = 2\text{H}_2\text{AlO}_3^- + 3\text{H}_2$	
$\text{Al}(\text{amalgam}) + 6\text{H}_2\text{O} = 2\text{Al}(\text{OH})_3 + 3\text{H}_2$	
$\text{Al}(\text{amalgam}) + 4\text{H}^+ + \text{NO}_3^- = \text{Al}^{+++} + \text{NO} + 2\text{H}_2\text{O}$	Dilute nitric forms $\text{NH}_4^+$
$2\text{Al} + \text{Fe}_2\text{O}_3 = \text{Al}_2\text{O}_3 + 2\text{Fe}$	Analogous reaction with many oxides and sulfides
$2\text{Al} + 3\text{X}_2 = 2\text{AlX}_3$	With halogens
$2\text{Al} + 6\text{S} = 2\text{Al}_2\text{S}_3$	At high temperature
$2\text{Al} + \text{N}_2 = 2\text{AlN}$	Slowly at high temperature
$6\text{Al} + 3\text{CO} = \text{Al}_4\text{C}_3 + \text{Al}_2\text{O}_3$	At high temperature

**18. Oxide and Hydroxide.**—The oxide occurs in nature as corundum. When colored red it is called ruby, and

when blue, sapphire. The color in the former is due to a trace of chromium, while that of the latter is attributed to iron and titanium. When it contains magnetite, it is known as emery. Artificial corundum, made by fusing the precipitated hydroxide in an electric furnace, is sold under the name "alundum," and artificial rubies and sapphires are now produced in large quantities. Corundum stands next to diamond and silicon carbide in hardness, and is used as an abrasive, and also in making refractory crucibles. The oxide is formed upon heating the hydroxide. Unless it has been ignited strongly, it will reabsorb water to form the hydroxide, and hence may be employed as a drying agent.

Both the tri- and mono-hydrates of aluminum oxide occur in two crystalline modifications:  $\alpha$ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , bay-erite;  $\gamma$ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , gibbsite;  $\alpha$ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , diaspore; and  $\gamma$ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , böhmite. The freshly precipitated gel appears to be hydrous  $\gamma$ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{HAlO}_2)$ ; upon aging this contains more or less of both of the tri-hydrates but the  $\gamma$ -modification is the stable form at ordinary temperatures. Bauxite,  $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  (formula indefinite) is the principal commercial ore. The hydroxide is amphoteric, and the following approximate values may be given for the basic and acidic dissociation constants:



$$K = 4 \times 10^{-13}.$$

The hydroxide is dissolved but slightly by ammonium hydroxide, especially in the presence of ammonium salt, to repress the concentration of hydroxide ion. The concentrations of hydroxide and hydrogen ions involved in the precipitation and solution of the hydroxide are indicated in Fig. 2. Soluble carbonates, sulfides, acetates, cyanides, and other salts of weak acids precipitate aluminum hydroxide by complete hydrolysis of both ions.

The pure oxide required for the electrolytic preparation of the metal is made from bauxite or other hydrated oxides. The mineral is first dissolved in sodium hydroxide to form a solution of sodium aluminate; and the hydroxide is then reprecipitated by passing in carbon dioxide, or by allowing the solution to stand in contact with crystallized  $\text{Al}(\text{OH})_3$ . In the latter case, the crystallized and insoluble form slowly precipitates (see Beryllium Hydroxide). Many attempts have been made to prepare the pure oxide from clay, but no commercial process has yet been developed.

**19. Aluminates.**—Sodium and potassium aluminates are soluble but highly hydrolyzed. Most of the aluminates are, however, insoluble. The meta aluminates of the  $+2$  ions,  $\text{M}(\text{AlO}_2)_2$ , occur as a mineral type known as spinels. Many complex aluminates exist, but few as simple ortho salts. The addition of ammonium hydroxide to a solution of aluminum and zinc salts precipitates aluminum hydroxide with some zinc aluminate. The formation of blue cobalt aluminate is mentioned under the analytical properties of aluminum. Calcium aluminate is an essential constituent of Portland cement (cf. **XIV—24**).

**20. Halides.**—The anhydrous halides may be prepared by the direct action of the halogen upon the metal, while solutions of the halides are formed by the action of the halogen acids upon the metal or hydroxide. Upon evaporation of the solutions, the halides may be obtained as highly hydrated compounds, e.g.,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ . When heated, the hydrates hydrolyze completely to the oxide and the halogen

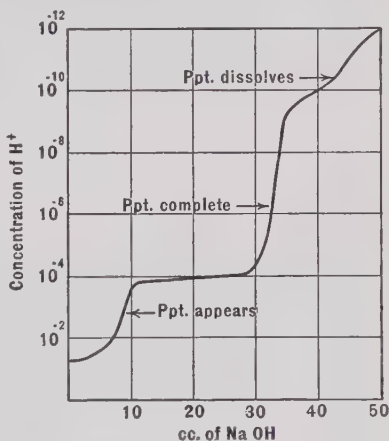
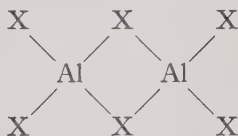


FIG. 2. Precipitation and solution of aluminum hydroxide in alkali.

acid, which is evolved. The anhydrous chloride is employed as a catalytic agent in many organic reactions. It sublimes without melting at ordinary pressures, the sublimation temperature being  $183^{\circ}$  at 750 mm. The aluminum halide gas molecules have the double formula  $\text{Al}_2\text{X}_6$  and their structure may be represented as two tetrahedra of halide ions with an edge in common, and aluminum atoms at the centers of the tetrahedra.



The halides form compounds with ammonia similar in nature to the hydrates, thus  $\text{AlCl}_3 \cdot 6\text{NH}_3$  forms at ordinary temperatures by the action of ammonia gas upon the salt. Aluminum fluoride exhibits strong tendencies to form complex salts, giving the radical,  $\text{AlF}_6^{---}$ , as in cryolite,  $\text{Na}_3\text{AlF}_6$ . These compounds are analogous to the aluminate, and owe their stability to the large value of  $ee'/(r + r')$  (cf. III—7) for aluminum and fluoride ions. The tendency of the other halides of aluminum to form complexes decreases with increasing weight.

**21. Sulfates.**—The sulfate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , may be crystallized with difficulty from solutions at ordinary temperatures. It is highly soluble, and gives an acid solution by hydrolysis. A 0.25*M* solution is about 0.5 per cent hydrolyzed, assuming that the hydrolysis reaction is  $\text{Al}^{+++} + \text{H}_2\text{O} = \text{Al}(\text{OH})^{++} + \text{H}^+$ . The sulfate is prepared from either bauxite or clay by treating with sulfuric acid. The latter reaction is:  $\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{SO}_4 = \text{Al}_2(\text{SO}_4)_3 + 2\text{H}_2\text{SiO}_4 + \text{H}_2\text{O}$ . The silicic acid is insoluble, and may be filtered off.

With the alkali sulfates, except lithium, and with ammonium, silver, and thallosulfates, aluminum sulfate forms isomorphous compounds of the general type,  $\text{MAl}(\text{SO}_4)_2$ .

$12\text{H}_2\text{O}$ , known as **alums**. The class is even more general, and the aluminum may be substituted by  $\text{Fe}^{+++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Mn}^{+++}$ ,  $\text{Ti}^{+++}$ , and other + 3 ions. The tendency of the alkali elements to form alums increases with increasing atomic weight; cesium forms more alums than the others and these are in general less soluble. The ammonium and potassium alums are the most important commercially. These alums are very soluble in hot water, but much less in cold, so that they may readily be purified by crystallization. Crystal structure data indicate that six of the water molecules form an octohedron about the aluminum ion and the other six water molecules occupy "cavities" in the lattice.

The principal uses of aluminum sulfate and alum depend primarily upon the hydrolysis of the aluminum ion, and may be divided into two classes: (1) those depending upon properties of hydrogen ion, and (2) those depending upon the properties of aluminum hydroxide. In the first class may be mentioned the use in baking powder to furnish acid to cause the liberation of carbon dioxide. The same reaction is employed in certain fire extinguishers, in which solutions of alum are caused to react with solutions of sodium bicarbonate containing organic substances capable of forming very stable foams. To the second class belong the uses as a mordant in dyeing, and as a clarifying agent for water. Aluminum hydroxide, formed by the addition of sodium carbonate or lime to alum or aluminum sulfate, is a very good absorbent for certain dyes, and also attaches itself to the fiber, thus serving to bind the dye to the material. **Mordants** of this nature are frequently necessary in dyeing cotton goods. Certain dyes may also be adsorbed on aluminum hydroxide to form pigments known as "**lakes.**" The action of alum in water clarification is again due to the adsorption of suspended material by the gelatinous precipitate. Alum is also used in sizing paper and in fireproofing fabric.

When heated it loses water and some sulfur trioxide; the product, known as "burnt alum," is used in medicine as an "astringent."

**22. Ultramarine.**—A complex sodium aluminum silicate and sulfide occurs in nature as the mineral lapis lazuli. When ground, it constitutes the blue pigment, ultramarine. The pigment is now manufactured by heating a mixture of clay, sodium sulfate, and carbon, and is much used for laundry blue, as a water color, and in neutralizing yellow tones in linen, starch, paper, and granulated sugar. It is stable toward alkalies, but evolves hydrogen sulfide with acids.

**23. Other Compounds of Aluminum.**—**Aluminum sulfide**,  $\text{Al}_2\text{S}_3$ , is formed by the reduction of metallic sulfides by aluminum at high temperatures. It is completely hydrolyzed in water. **Aluminum acetate**,  $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$ , has many uses similar to those of the sulfate. It may be prepared from the sulfate by metathesis with barium acetate. **Kaolin**, the hydrated silicate, is further discussed under silicon.

**24. Analytical Properties of Aluminum Ion.**—Aluminum ion is colorless, and has a slightly bitter astringent taste. It forms an insoluble amphoteric hydroxide as already discussed. The orthophosphate,  $\text{AlPO}_4$ , is insoluble, and precipitates upon the addition of a soluble phosphate and ammonium hydroxide to aluminum ion. The separation of aluminum from other positive ions, and its identification as the hydroxide, is outlined in the general scheme of analysis (Append. VI). Precipitated aluminum hydroxide is often confirmed by moistening the precipitate with a drop of cobalt nitrate solution and igniting at red heat. A blue residue (cobalt aluminate) indicates the presence of aluminum. The test is capable of detecting 0.2 mg. of aluminum. It is necessary in carrying out the test to have the aluminum oxide in excess, as otherwise the color observed is obscured by the black cobalt oxide. The test



is not satisfactory if sodium or potassium salts are occluded in the precipitate in any large amounts.

The formation of a bright red lake (cf. Par. 21) with the dye aluminon ( $\text{NH}_4$  salt of aurin tricarboxylic acid) may also be used to detect aluminum. A satisfactory method of carrying out the test is to use an aluminum free filter paper treated with a dilute solution of the dye and ammonium acetate. A drop of test solution is placed on the paper and held for a few seconds in the fumes from an ammonium hydroxide bottle. Red color indicates aluminum.

Complex aluminates may be dissolved by fusion in a platinum dish with potassium acid sulfate or with sodium carbonate, followed by extraction with hydrochloric acid. Silica is removed by evaporating to dryness, boiling again with hydrochloric acid, and filtering.

Aluminum is generally determined in quantitative analysis by precipitating as the hydroxide and weighing as the oxide.

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# Chapter VII

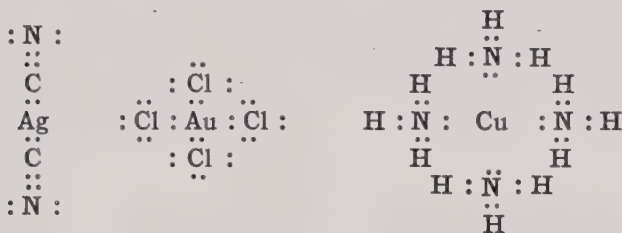
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## SUBGROUP I. COPPER, SILVER, AND GOLD

1. The elements of Subgroup I, copper, Cu (cuprum), silver, Ag (argentum), and gold, Au (aurum), differ markedly in properties from the elements of the main group. Unlike the alkalis they are "noble" metals and are not readily oxidized. This property may be correlated (cf. **III—5**) with the higher boiling points of the metals, indicating greater difficulty in separating their atoms from each other, and with the larger ionization potentials of the gaseous atoms (Table I). Their oxides, of the type  $M_2O$ , are much less basic than the alkali oxides, a fact which is related to the smaller size of the ions (cf. Table I, also **III—7**). These elements also form certain compounds in which they have oxidation states greater than + 1; in fact, the ions of + 2 copper and + 3 gold are in general more stable in respect to reducing agents than the ions of the + 1 state. The outer electron shell of the kernel is not of the noble gas type, but contains 18 electrons, and these higher states exist through the possibility of removing one or two electrons from this shell. This process is impossible in the case of the main group elements, since the energies of their kernel electrons are very much greater.

2. The ions of the subgroup elements possess the property of forming very stable complexes, such as  $Cu(NH_3)_4^{++}$ ,  $Ag(CN)_2^-$ ,  $AuCl_4^-$ . This property is in general strongly exhibited by all ions with more than eight electrons in the outer shell of the kernel, and may be considered as due to

the ability of these positive ions to form definite electron pair bonds. These complexes have been called **coordination compounds**, and the number of groups or ions held by the positive ion is termed its **coordination number**. The electrons of the bond are of course supplied by the coordinating group.



Silver cyanide ion

Chloraurate ion

Cupric ammonia ion

Fluoride ion, which exhibits strong tendencies to form ionic complexes with the smaller ions such as aluminum, does not readily form complexes with the subgroup elements, because its electrons are held so firmly that they are not readily shared in bond formation. The stability of the complexes and also the solubility of the compounds of the ions appear to be related to the electrical distortion or polarization of the negative ions. This relation is illustrated by the following comparison of the solubilities of a number of silver salts with the indices of refraction of the negative ions, which may be taken as a measure of the polarization.

	F <sup>-</sup>	O <sup>-2</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	S <sup>-2</sup>
Solubility of silver salt moles/liter...	13.5	$2 \times 10^{-4}$	$9 \times 10^{-6}$	$6 \times 10^{-7}$	$1 \times 10^{-8}$	$< 10^{-8}$
Index of refraction of negative ion per g. atom .....	2.5	7.0	9.0	12.7	19.2	20.0

Moreover, the interatomic distances correspond in general to those for covalent bonds (cf. Appendix) rather than

those for the ionic radii. Both the  $\text{AuCl}_4^-$  and  $\text{Cu}(\text{NH}_3)_4^{++}$  given above are square planar structures instead of the customary tetrahedra, which result from a combination of *s* and *p* orbitals. The square structures are formed by a combination of one *s*, two *p*, and one *d* orbitals.

3. The basic nature of the oxide (comparing the +1 oxides) increases with increasing size of the atom, but the electropositive nature of the metal, i.e. ease of oxidation, decreases; gold being one of the most noble metals. The metals are all excellent electrical conductors.

## COPPER

4. **Occurrence.**—Copper frequently occurs in the free state. As a rule such deposits are small, but in the Lake Superior region masses of native copper have been found weighing many tons. The copper ores may be classified as: (1) sulfide ores, the more important being chalcopyrite,  $\text{CuFeS}_2$ , bornite, approximately  $\text{Cu}_3\text{FeS}_3$ , chalcocite,  $\text{Cu}_2\text{S}$ , and indigo copper,  $\text{CuS}$ ; (2) oxidized ores, consisting of the oxides and their compounds with negative elements, such as cuprite,  $\text{Cu}_2\text{O}$ , melaconite,  $\text{CuO}$ , malachite,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ , azurite,  $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ , chrysocolla,  $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$ , and atacamite,  $\text{CuCl}_2 \cdot 3\text{CuO} \cdot 3\text{H}_2\text{O}$ . The average percentage of copper in igneous rocks is estimated as  $1.0 \times 10^{-4}$ .

5. **Metallurgy.**—The methods employed in winning copper from its ores vary greatly with the type of ore. With native copper the rock is crushed, the copper concentrated by mechanical methods, and the metal purified by melting with a flux to remove the remaining gangue. High grade oxidized ores are smelted by heating in a furnace with a mixture of coke and suitable fluxes. Low grade ores may be worked by extraction of the copper with ammonia or other solvents. About 70 per cent of the copper in the United States is produced from sulfide ores. The procedure is somewhat complicated because the sulfide is not

TABLE I  
ATOMIC AND PHYSICAL PROPERTIES

ELEMENT	COPPER	SILVER	GOLD
Symbol.....	Cu	Ag	Au
Atomic number.....	29	47	79
Atomic weight.....	63.57	107.880	197.2
Isotopes.....	63, 65	107, 109	197
Number of electrons in various quantum levels, 1st.....	2	2	2
2d.....	8	8	8
3d.....	18	18	18
4th.....	1	18	32
5th.....	—	1	18
6th.....	—	—	1
Color of metal.....	red	silver	yellow
Density.....	8.92	10.5	19.3
Melting point, ° C.....	1,083	960.5	1,063
Boiling point, ° C.....	2,310	1,950	2,600
Tensile strength, lb./sq. in.....	60,000	42,000	20,000
Specific resistance at 20°, ohm/cm. $\times 10^6$ ...	1.72	1.59	2.44
Ionization potential of gaseous atom, volts...	7.68	7.54	9.18
Radius of $M^+$ in solids, $\times 10^8$ cm.....	0.96	1.26	1.37
Potential of electrode, $M = M^+(aq) + e^-$ (hydrogen electrode = 0).....	- 0.522	- 0.799	ca - 1.68

readily reduced, and also because of the difficulty in removing the large amount of iron which is always present. The steps in the process are (1) concentration of the ore (only with low grade ores), (2) roasting, (3) formation of "copper matte," largely  $Cu_2S$  and  $FeS$ , (4) reduction of the matte to "blister copper," (5) refining of the "blister copper."

The concentration of low grade ores is now usually carried out by the "flotation" methods. The ore is ground with oil and water. The sulfide particles are wet by the oil and the earthy particles by the water. The mass is added to a larger amount of water containing a foaming agent and beaten or blown into a foam. The sulfide particles collect at the surface of the bubbles and are carried off with the foam, while the earthy particles, or "gangue," settle to the bottom. It is claimed that the method will

remove as much as 95 per cent of the metal from an ore containing as low as 2 per cent copper.

The roasting step serves to remove volatile oxides of arsenic and antimony, and to oxidize part of the sulfides to the metallic oxides and sulfur dioxide. The next step is the formation of the copper matte by heating the ore with addition of sand or calcium carbonate in the proper proportion to form easily fusible calcium silicate slag. This is carried out either in a reverberatory furnace in which hot flames of burning coal dust are played upon the surface of the charge, or in a blast furnace where a blast of air is blown through the charge. In the latter case coke is added to the mixture, and its combustion supplies the heat. The temperature is kept high enough to melt the charge, and the heavier mixture of the molten sulfides settles beneath the lighter slag. During the process some of the iron is removed as iron silicate, and some of the sulfur is oxidized to sulfur dioxide. The matte consists of cuprous and ferrous sulfides. The next step is now generally carried out in the so-called copper converter, a barrel shaped vessel provided with a number of blast pipes. Air is blown through the charge, to which sand has been added, and the ferrous sulfide is converted to ferrous oxide, which forms ferrous silicate:  $2\text{FeS} + 3\text{O}_2 = 2\text{FeO} + 2\text{SO}_2$ , and  $\text{FeO} + \text{SiO}_2 = \text{FeSiO}_3$ . When the iron sulfide is all oxidized, the blast is stopped and the slag poured off. The blast is then renewed and metallic copper formed by the oxidation of the sulfur:  $\text{Cu}_2\text{S} + \text{O}_2 = 2\text{Cu} + \text{SO}_2$ . The copper is poured into molds, and upon cooling evolves some dissolved sulfur dioxide, which gives the surface a "blistered" appearance.

About 70 per cent of the blister copper in the United States is refined by the electrolytic method, wherein the crude metal is made the anode in a cell containing an acid solution of copper sulfate. A thin plate of pure copper serves as the cathode. By regulating the potential drop



across the cell, it is possible to dissolve copper and the baser metals at the anode, leaving behind the more noble metals, such as silver, gold, and platinum as an "anode sludge." The difference in the electro-potential of copper and the base metals, iron, zinc, lead, and nickel, is sufficient so that in the acid solution copper is preferentially deposited at the cathode with a purity of approximately 99.9 per cent.

In the older methods of refining blister copper, the metal is heated in a silica lined vessel, with agitation to bring about oxidation of the base metals by the air. The basic oxides then form a slag with the silica lining. The principal impurity now present is cuprous oxide which is soluble in molten copper; so after skimming off the slag, the metal is stirred with a pole of green wood, and the hot hydrocarbons liberated from the wood reduce the cuprous oxide. The process does not give as pure copper as the electrolytic method, nor does it render possible the recovery of the more noble metals.

**6. The Metal.**—The more important physical properties are given in Table I. The yearly production of copper is over two million tons, of which the United States produces about 40 per cent. Its principal use, due to its high electrical conductivity and good ductility, is in electrical transmission. For this purpose it must be extremely pure, since the presence of a few tenths of a per cent of certain impurities, especially arsenic, greatly increases the resistance. Because of its high thermal conductivity and comparative inertness, it is used in boilers, water heaters, cooking utensils, steam pipes, etc. It is used in the electrotyping processes now generally employed in reproducing engravings and printing books. A plaster or wax cast is made of each page of type, the cast is coated with graphite to render it conducting, and copper is then deposited upon the cast electrolytically. The deposit of copper is then removed and strengthened by filling the back with lead.

A summary of the composition of the more important

alloys of copper is given in Table II. Bronze is much harder than copper, and also more readily cast into molds. Aluminum bronze resembles gold in color, and is used in gilt paint. Aluminum silicon bronze is quite resistant to corrosion and has a tensile strength about double that of pure copper. Brass foil is often used as a substitute for gold leaf. German silver, as its name indicates, resembles silver in appearance. It is a very poor conductor of heat. Phosphor bronze is employed in bearings. Constantan has a high and very reproducible thermoelectric force against copper, and the copper-constantan thermo-couple is used in the measurement of temperature.

TABLE II  
COPPER ALLOYS

Brass.....	60-90 Cu, 10-40 Zn
Bronze.....	80 Cu, 15 Sn, 5 Zn
Aluminum bronze.....	90 Cu, 10 Al
Aluminum silicon bronze.....	91 Cu, 7 Al, 2 Si
Phosphor bronze.....	80 Cu, 10 Sn, 9 Sb, 1 P
Manganese bronze.....	70-95 Cu, 5-30 Mn
Silicon bronze.....	95 Cu, 5 Si
Gunmetal.....	90 Cu, 10 Sn
Bell metal.....	78 Cu, 22 Sn
Constantan.....	60 Cu, 40 Ni
Manganin.....	82 Cu, 15 Mn, 3 Ni
German silver.....	52-60 Cu, 25 Zn, 15-22 Ni

TABLE III  
REACTIONS OF THE METAL

$2\text{Cu} + \text{O}_2 = 2\text{CuO}$	Rapid at about 300°
$4\text{Cu} + \text{O}_2 = 2\text{Cu}_2\text{O}$	At about 1,000°
$\text{Cu} + \text{F}_2 = \text{CuF}_2$	Also with $\text{Cl}_2$ and $\text{Br}_2$ . $\text{I}_2$ forms $\text{CuI}$ .
$2\text{Cu} + \text{S} = \text{Cu}_2\text{S}$	Upon heating. Also with Se, Te, P
$\text{Cu} + 2\text{H}^+ + \frac{1}{2}\text{O}_2 = \text{Cu}^{++} + \text{H}_2\text{O}$	With any acid not too weak
$\text{Cu} + 4\text{NH}_3 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = \text{Cu}(\text{NH}_3)_4(\text{OH})_2$	
$2\text{Cu} + \text{O}_2 + \text{CO}_2 + \text{H}_2\text{O} = \text{Cu}_2\text{CO}_3(\text{OH})_2$	Corrosion in air
$\text{Cu} + 2\text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$	Hot conc. acid
$\text{Cu} = \text{Cu}^{++} + 2e^-$	In general with oxidizing agents of potential greater than -0.34 volt, e.g. $\text{HNO}_3$

**7. Oxidation States.**—Copper forms compounds in which its oxidation state is + 1 (cuprous), + 2 (cupric), and (a few unstable compounds) + 3. Important potential values dealing with the oxidation and reduction of cuprous and cupric compounds have been summarized in Table IV.

TABLE IV  
OXIDATION REDUCTION POTENTIALS OF COPPER

	VOLTS <sub>25°</sub>
$\text{Cu} + 2\text{S}^{--} = \text{Cu}_2\text{S} + 2e^-$ .....	+ 0.95
$\text{Cu} + \text{S}^{--} = \text{CuS} + 2e^-$ .....	+ 0.76
$2\text{Cu} + 2\text{OH}^- = \text{Cu}_2\text{O} + \text{H}_2\text{O} + 2e^-$ .....	+ 0.36
$\text{CNS}^- + \text{Cu} = \text{CuCNS} + e^-$ .....	+ 0.27
$\text{Cu} + 2\text{OH}^- = \text{Cu}(\text{OH})_2 + 2e^-$ .....	+ 0.21
$\text{Cu} + \text{I}^- = \text{CuI} + e^-$ .....	+ 0.19
$2\text{NH}_3 + \text{Cu} = \text{Cu}(\text{NH}_3)_2^+ + 2e^-$ .....	+ 0.11
$\text{Cu}_2\text{O} + 2\text{OH}^- + \text{H}_2\text{O} = 2\text{Cu}(\text{OH})_2 + 2e^-$ .....	+ 0.09
$4\text{NH}_3 + \text{Cu} = \text{Cu}(\text{NH}_3)_4^{++} + 2e^-$ .....	+ 0.05
$\text{Cu} + \text{Br}^- = \text{CuBr} + e^-$ .....	- 0.03
$\text{Cu} + \text{Cl}^- = \text{CuCl} + e^-$ .....	- 0.12
$\text{Cu}^+ = \text{Cu}^{++} + e^-$ .....	- 0.17
$\text{Cu} = \text{Cu}^{++} + 2e^-$ .....	- 0.34
$\text{Cu} = \text{Cu}^+ + e^-$ .....	- 0.52
$\text{CuCl} = \text{Cu}^{++} + \text{Cl}^- + e^-$ .....	- 0.57
$\text{CuI} = \text{Cu}^{++} + \text{I}^- + e^-$ .....	- 0.88
$\text{Cu}^{++} = \text{Cu}^{+++} + e^-$ .....	- 1.8

In the case of soluble salts giving the ions  $\text{Cu}^+$  and  $\text{Cu}^{++}$ , it is easier to oxidize the metal to the cupric state than to the cuprous, and this also means that the equilibrium,  $2\text{Cu}^+ = \text{Cu} + \text{Cu}^{++}$ , favors the reactions as written: e.g. cuprous nitrate will decompose into cupric nitrate and copper. Also the reduction of cupric ion in such solutions will yield the metal and not cuprous ion.

However, cuprous ion forms many very slightly soluble salts and very stable complex ions, and with many of these the above equilibria are reversed. The following are a number of important examples:

(a) *Halides.* Cupric chloride and bromide are reduced, e.g. by electrolysis or by the metal, to the cuprous salt. The addition of iodide to cupric ion results in the liberation of iodine:  $\text{Cu}^{++} + 2\text{I}^- = \text{CuI} + \frac{1}{2}\text{I}_2$ .

(b) *Cyanide*. Cupric ion and cyanide give cuprous cyanide ion and cyanogen (or cyanate in ammonia solutions):  $2\text{Cu}^{++} + 8\text{CN}^- = 2\text{Cu}(\text{CN})_3^{--} + \text{C}_2\text{N}_2$ . This complex is so stable that the metal will dissolve in hydrogen cyanide, in spite of its weakness, with the evolution of hydrogen:  $\text{Cu} + 3\text{HCN} = \text{H}_2\text{Cu}(\text{CN})_3 + \frac{1}{2}\text{H}_2$ .

(c) *Oxide*. The reduction of cupric compounds in alkaline solution gives cuprous oxide,  $\text{Cu}_2\text{O}$ . This is the basis for the common test for sugar (specifically dextrose). An alkaline solution of copper sulfate and Rochelle salts,  $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ , known as **Fehling's solution**, will give a red coloration with extremely small quantities of dextrose, due to the precipitation of  $\text{Cu}_2\text{O}$ .

(d) *Reduction upon Heating*. Cupric compounds are in general unstable in respect to the cuprous upon heating.  $2\text{CuO} = \text{Cu}_2\text{O} + \frac{1}{2}\text{O}_2$ . The partial pressure of oxygen becomes appreciable above  $900^\circ\text{C}$ . However, the two oxides appear to form a solid solution in each other so that the partial pressure depends both upon the temperature and the concentration of the two oxides. Cupric sulfide decomposes at red heat:  $2\text{CuS} = \text{Cu}_2\text{S} + \text{S}$ . The cupric halides decompose according to the equation:  $2\text{CuX}_2 = 2\text{CuX} + \text{X}_2$ . Cupric fluoride decomposes around  $500^\circ$ , and the chloride and bromide at somewhat lower temperatures. The iodide is not stable even at room temperatures.

7. Powerful oxidizing agents, in alkaline solution, oxidize copper to the +3 state, probably forming  $\text{CuO}_2^-$ . The calcium salt may be precipitated. This compound is very unstable; it tends to evolve oxygen and it reacts readily with reducing agents.

8. **Cuprous Ion and Cuprous Compounds**.—Cuprous compounds are prepared from the cupric by methods based upon the reactions discussed in the preceding paragraph. The ion, and in general its complex ions, are colorless. The **oxide** occurs in nature. It has a fine red color, and for that reason is employed in making ruby glass and in coloring

porcelain. For the arrangement of the ions in the crystal lattice see Appendix V. It is insoluble in water and alkalis. Alkalies precipitate yellow orange hydrous cuprous oxide from cuprous compounds. Upon heating, it is transformed to the red modification. It reacts with sulfuric, nitric, and hydrofluoric acids to give copper and the cupric salt. It dissolves in ammonia, alkali cyanide, and hydrochloric acid to form the complex ions:  $\text{Cu}(\text{NH}_3)_2^+$ ,  $\text{Cu}(\text{CN})_3^{--}$ , and  $\text{CuCl}_2^-$ . The cuprous chloride and ammonia solution is oxidized by oxygen to the cupric compound, and advantage is sometimes taken of this in removing oxygen from gas:  $2\text{Cu}(\text{NH}_3)_2^+ + 2\text{NH}_4\text{OH} + \frac{1}{2}\text{O}_2 = 2\text{Cu}(\text{NH}_3)_4^{++} + 2\text{OH}^- + \text{H}_2\text{O}$ . The **chloride**, **bromide**, and **iodide** are slightly soluble in water, the solubility decreasing in the order given, as with the corresponding silver halides. They are all soluble in excess of the halide ion: e.g.  $\text{CuBr} + \text{Br}^- = \text{CuBr}_2^-$ . The chloride is hydrolyzed in boiling water:  $2\text{CuCl} + \text{H}_2\text{O} = \text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{Cl}^-$ . A solution of chlorocuprous acid,  $\text{HCuCl}_2$ , is employed in gas analysis to absorb carbon monoxide. The reaction is apparently due to the formation of a rather unstable carbonyl cuprous chloride,  $\text{CuCl} \cdot \text{CO} \cdot 2\text{H}_2\text{O}$ . A solution of cuprous ammonia carbonate is sometimes employed in place of the chloride for the same purpose. The chloride is soluble in cyanide and in ammonia, with the formation of the complex ions. The cyanide ion,  $\text{Cu}(\text{CN})_3^{--}$ , gives the smallest concentration of cuprous ion of any of the cuprous compounds. **Cuprous sulfide** is formed by heating together copper and sulfur, by roasting cupric sulfide, and by reduction of cupric sulfide by hydrogen. It may also be precipitated from a solution of chlorocuprous acid by the action of hydrogen sulfide. It is soluble in hot nitric acid with the oxidation of both the copper and sulfur. **Cuprous thiocyanate**,  $\text{CuSCN}$ , is also insoluble.

**9. Cupric Ion.**—Cupric ion in dilute aqueous solution probably exists as  $\text{Cu}(\text{H}_2\text{O})_4^{++}$ , and the characteristic blue color of its solutions is probably due to this complex. Its

most important slightly soluble compounds are the black oxide,  $\text{CuO}$ ; the green hydroxide,  $\text{Cu}(\text{OH})_2$ ; the green basic carbonate,  $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ; the black sulfide,  $\text{CuS}$ ; and red-brown ferrocyanide,  $\text{Cu}_2\text{Fe}(\text{CN})_6$ . The most important complex ions are the deep blue cupric ammonia,  $\text{Cu}(\text{NH}_3)_4^{++}$ ; chlor and brom cuprates,  $\text{CuCl}_4^{--}$ ,  $\text{CuBr}_4^{--}$  (respectively green and brown); and tartrate,  $\text{Cu}(\text{C}_4\text{H}_4\text{O}_6)_2^{--}$ . The soluble cupric salts of strong acids are all slightly acid by hydrolysis.

**10. Cupric Oxide and Hydroxide.**—The addition of hydroxide ion to a cold solution of cupric ion gives a light bluish green gelatinous precipitate of the hydroxide, but in hot solutions the black oxide is formed. The oxide does not absorb water to form the hydroxide. The hydroxide is a weak base.  $\text{Cu}(\text{OH})_2 = \text{Cu}^{++} + 2\text{OH}^-$ ,  $K = 5.6 \times 10^{-20}$ . It is not soluble in dilute alkalies, but does dissolve somewhat in 6*N* to 18*N*  $\text{NaOH}$ , forming deep blue solutions of cuprate,  $\text{Cu}(\text{OH})_2 + 2\text{OH}^- = \text{CuO}_2^{--} + 2\text{H}_2\text{O}$ ,  $K = 1.2 \times 10^{-3}$ . The sodium cuprate,  $\text{Na}_2\text{CuO}_2$ , may be precipitated from the concentrated alkaline solutions. The hydroxide is soluble in ammonium hydroxide, forming the complex ammonia ion, and in tartrate, forming the complex tartrate (**Fehling's solution**). The oxide is also formed by heating the carbonate or nitrate. At moderately high temperatures, it oxidizes hydrogen, forming water and copper. In quantitative organic analysis, mixtures of the oxide and organic compound are heated to effect the oxidation of the combined carbon and hydrogen to carbon dioxide and water.

**11. Cupric Halides.**—The fluoride, chloride, and bromide are readily soluble. As mentioned above, the iodide is unstable. The concentrated solution of the chloride is green, and of the bromide, brown. The color appears to be due to existence of part of the copper in the complex ions,  $\text{CuCl}_4^{--}$  (green), and  $\text{CuBr}_4^{--}$  (brown). Upon electrolysis, copper moves toward both the cathode and anode. When the con-



centrated solutions are diluted, the blue of the  $\text{Cu}(\text{H}_2\text{O})_4^{++}$  again predominates. The solid halides absorb ammonia gas to form compounds, such as  $\text{CuCl}_2 \cdot 6\text{NH}_3$ . These compounds, of course, give the complex ammonia ion upon solution.

**12. Cupric Sulfate.**—The sulfate is the most important copper salt. The anhydrous salt is colorless, but it readily absorbs water to form the blue pentahydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , known as “blue vitriol.” The five molecules of water of hydration may be successively replaced by ammonia. The sulfate is prepared commercially by roasting the sulfide, either to form the sulfate, which may be extracted with water, or to form the oxide, which may be dissolved in sulfuric acid. A 0.2*N* solution is 0.057 per cent hydrolyzed at 25° C. From solutions of copper sulfate and the alkali sulfates, double salts, such as  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , may be crystallized. Upon slow addition of alkali to copper sulfate solution, a number of insoluble basic sulfates are formed, for example,  $\text{Cu}_5(\text{SO}_4)_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ . Basic sulfates, made by mixing copper sulfate and slaked lime, are used under the name of “**Bordeaux mixture**” as a fungicide. Copper sulfate is used in calico printing, in electroplating, and electrotyping, and as an electrolyte in the gravity battery. Copper is very poisonous to lower organisms, especially algae, and is used in swimming pools and water works to prevent the growth of such organisms.

**13. Cupric Sulfide.**—The brownish black sulfide is precipitated from cupric solutions by the action of hydrogen sulfide, even in the presence of high concentrations of acid. When precipitated from neutral solution, it may contain some cuprous sulfide. It is soluble in hot 2*N*  $\text{HNO}_3$  because of the oxidation of the sulfur, and in cyanide ion because of the formation of  $\text{Cu}(\text{CN})_3^{--}$ . The sulfide is slightly soluble in ammonium polysulfide, probably through the formation of thiocuprates.

**14. Other Cupric Salts.**—The **nitrate** crystallizes as blue hexahydrate. Because of the smaller solubility of the hy-

dioxide, the normal carbonate does not exist, but two **basic carbonates**, azurite,  $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ , and malachite,  $\text{Cu}_2\text{CO}_3(\text{OH})_2$ , occur in nature. The latter is the green coating which forms on copper vessels through the action of oxygen and carbonic acid of the air. A **basic acetate**, verdigris,  $\text{Cu}_3(\text{C}_2\text{H}_3\text{O}_2)_4(\text{OH})_2$ , is used as a green pigment. It is formed by the action of air upon copper in the presence of acetic acid. A mixed acetate and arsenite,  $\text{Cu}_4(\text{C}_2\text{H}_3\text{O}_2)_2(\text{AsO}_3)_2$ , **Paris green**, is used as an insecticide. Copper ferrocyanide,  $\text{Cu}_2\text{Fe}(\text{CN})_6$ , may be formed as a brown gelatinous precipitate. It has been used in the preparation of semi-permeable membranes for studying osmotic pressure. **Copper phosphate**,  $\text{Cu}_3(\text{PO}_4)_2$ , is insoluble and is precipitated, together with basic phosphates, upon the addition of diammonium phosphate to a solution of copper sulfate.

**15. Analytical.**—Copper is recognized qualitatively by the intense blue color of the ammonia complex, and by the precipitation of the sulfide by hydrogen sulfide in acid solution. Nickel also gives a blue ammonia complex, but its sulfide is not precipitated in acid solution. A strip of iron in a not too acid copper solution will be coated with metallic copper. This is frequently a convenient and delicate test. The detailed methods of separation are indicated in Appendix VI. Copper is often determined quantitatively by the electrolytic precipitation of the metal in acid solution upon an accurately weighed cathode. This method affords a separation from the baser metals as well. A number of reactions are of importance in quantitative determinations. (a)  $2\text{Cu}^{++} + 5\text{I}^- = 2\text{CuI} + \text{I}_3^-$ . The liberated iodine is titrated with standardized thiosulfate. Other oxidizing agents such as ferric ion must be removed. (b)  $2\text{Cu}(\text{NH}_3)_4^{++} + 7\text{CN}^- + \text{H}_2\text{O} = 2\text{Cu}(\text{CN})_3^{--} + \text{CNO}^- + 2\text{NH}_4^+ + 6\text{NH}_3$ . The ammonia solution is titrated with standardized cyanide to the disappearance of the blue color. This method is not as accurate as the iodide reaction.

(c)  $2\text{Cu}^{++} + 2\text{CNS}^- + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{CuCNS} + 4\text{H}^+ + \text{SO}_4^{--}$ . The precipitate may be ignited and weighed as  $\text{Cu}_2\text{S}$ , or titrated with iodate in the presence of concentrated hydrochloric acid:  $4\text{CuCNS} + 7\text{IO}_3^- + 14\text{H}^+ + 14\text{Cl}^- = 4\text{Cu}^{++} + 4\text{SO}_4^{--} + 7\text{ICl}_2^- + 4\text{HCN} + 5\text{H}_2\text{O}$ .

## SILVER

**16. Occurrence.**—Native, or free silver is an important source of the element. It is usually alloyed with other of the noble metals. The most important naturally occurring compound is the sulfide, argentite, or silver glance,  $\text{Ag}_2\text{S}$ . It frequently occurs in solid solution with copper and lead sulfide, and as the sulfo-antimonite,  $\text{Ag}_3\text{SbS}_3$ , and arsenite,  $\text{Ag}_3\text{AsS}_3$ . The selenides and tellurides also occur. Silver chloride,  $\text{AgCl}$ , called horn silver, is an ore of some importance, and often contains the bromide and iodide in small amounts. The sulfate also occurs, being formed through the oxidation of the sulfide. The average percentage of silver in igneous rocks is estimated as  $10^{-8}$ .

**17. Metallurgy.**—The recovery of silver from copper ores has been mentioned. Much of the lead smelted from lead sulfide contains silver. This is now recovered by Parke's process, which is essentially an extraction of the silver from the molten lead by means of zinc. Solid zinc is but slightly soluble in lead at temperatures just above the melting point of the latter. However, silver at these temperatures is about 3,000 times more soluble in the zinc than in the molten lead. Hence zinc in small amounts, usually 0.8 to 1.5 per cent, is stirred with the molten lead, and the greater portion of the silver is extracted. The zinc is removed from the silver by distillation. The small amount of lead present is removed by oxidation and absorption of the lead oxide on a cupel of bone ash.

The extraction of silver from comparatively pure silver ore is accomplished either by (1) amalgamation, or (2)

leaching processes. The first depends upon the conversion of silver sulfide into chloride by copper chloride,  $\text{Ag}_2\text{S} + \text{Cu}^{++} + 2\text{Cl}^- = 2\text{AgCl} + \text{CuS}$ ; and the decomposition of the chloride by mercury,  $\text{AgCl} + \text{Hg} = \text{Ag (amalgam)} + \text{HgCl}$ . The silver is recovered from the amalgam by distillation of the mercury.

A number of leaching processes have been employed. A sulfide ore may be roasted to convert the sulfide into sulfate, which may then be extracted with water. Or the sulfide may be roasted with salt to convert it into chloride, which is then leached, either with concentrated brine, the solubility being due to the formation of  $\text{AgCl}_2^-$ , or with thiosulfate, forming the complex  $\text{Ag}(\text{S}_2\text{O}_3)_2^{--}$ . However, solutions of the alkali cyanides are now generally employed, as the metal and all of its compounds are readily dissolved by this reagent in the presence of air:  $4\text{Ag} + 8\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{Ag}(\text{CN})_2^- + 4\text{OH}^-$ ;  $\text{Ag}_2\text{S} + 4\text{CN}^- + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = 2\text{Ag}(\text{CN})_2^- + \text{S} + 2\text{OH}^-$ ;  $\text{AgCl} + 2\text{CN}^- = \text{Ag}(\text{CN})_2^- + \text{Cl}^-$ . The silver is precipitated from the cyanide solution by zinc or aluminum.

**18. The Metal.**—The more important physical constants have been given in Table I. Silver is the most lustrous of all the metals. In thermal and electrical conductivity it also ranks among the first. It is but little inferior to gold in malleability and ductility. Silver melted in air always has a blistered surface upon cooling, due to the evolution of dissolved oxygen during solidification. The solubility of oxygen under 1 atmosphere pressure at the melting point is 20 volumes per volume of the metal. The cooled solid silver still contains 0.75 volume of oxygen.

The annual production of silver is about 9,000 tons. Silver coins are generally 90 per cent silver with 10 per cent copper to increase the hardness. Jewelry usually contains 20 per cent of copper. The electroplating industry consumes a large proportion of the metal produced. The object to be coated is made the cathode in a cell containing a solution

TABLE V  
REACTIONS OF THE METAL

$2\text{Ag} + \frac{1}{2}\text{O}_2 = \text{Ag}_2\text{O}$	At 200° with $\text{O}_2$ under pressure
$2\text{Ag} + \text{X}_2 = 2\text{AgX}$	X denotes any halogen
$2\text{Ag} + \text{S} = \text{Ag}_2\text{S}$	Also with Se and Te
$2\text{Ag} + 2\text{H}_2\text{SO}_4 = \text{Ag}_2\text{SO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$	Hot concentrated acid
$2\text{Ag} + 2\text{H}^+ + 2\text{Cl}^- + \frac{1}{2}\text{O}_2 = 2\text{AgCl} + \text{H}_2\text{O}$	
$2\text{Ag} + \text{H}_2\text{O} + 4\text{CN}^- + \frac{1}{2}\text{O}_2 = 2\text{Ag}(\text{CN})_2^- + 2\text{OH}^-$	
$\text{Ag} = \text{Ag}^+ + e^-$	See oxidation reduction table

of sodium silver cyanide,  $\text{NaAg}(\text{CN})_2$ , as electrolyte. The cyanide complex, which gives a very low concentration of silver ion, yields a much firmer deposit than solutions having a higher concentration of the silver ion. Frosted silver ornaments are obtained by roasting the object, made of the ordinary silver-copper alloy, to oxidize the copper on the surface to the oxide; this is dissolved in sulfuric acid, leaving a layer of pure white silver. Silver mirrors are formed by precipitating the metal from a highly alkaline solution containing the silver ammonia complex ion by the aid of some organic reducing agent, such as glucose or formaldehyde. Approximately 150 tons of silver are used yearly in the production of photographic supplies.

**19. Stability of Silver Compounds.**—Silver ion is colorless. It forms such a very large number of slightly soluble salts and complexes that it is desirable to systematize the chemistry of these substances by arranging the more important in a list in order of decreasing concentration of silver ion in equilibrium with the solid or complex ion, and a 1M concentration of the ion or complex forming molecule. For salts of the types  $\text{Ag}_2\text{X}$  or  $\text{AgY}$  this is not necessarily the order of the solubility in pure water because of the square of the  $\text{Ag}^+$  concentration enters into the constant for the  $\text{Ag}_2\text{X}$ . The order is  $\text{Ag}_2\text{SO}_4$ ,  $\text{AgAc}$ ,  $\text{AgNO}_2$ ,  $\text{Ag}_2\text{CO}_3$ ,  $\text{Ag}_2\text{C}_2\text{O}_4$ ,  $\text{Ag}_2\text{CrO}_4$ ,  $\text{Ag}(\text{NH}_3)_2^+$ ,  $\text{Ag}_2\text{O}$ ,  $\text{Ag}(\text{SO}_3)_2^{---}$ ,  $\text{AgCl}$ ,  $\text{AgCNS}$ ,  $\text{AgBr}$ ,  $\text{Ag}(\text{SiO}_3)_2^{---}$ ,  $\text{AgCN}$ ,  $\text{AgI}$ , and  $\text{Ag}_2\text{S}$ . Any

substance in the list may be formed at the expense of any substance preceding it. Thus silver iodide may be formed from the chloride:  $\text{AgCl} + \text{I}^- = \text{AgI} + \text{Cl}^-$ . Substances which are close together in the list may be present together in equilibrium at appreciable concentrations of both. Thus silver bromide is partially soluble in ammonium hydroxide, and the reaction is easily reversible, depending upon the concentration of ammonia and bromide. The dissociation constant for the ammonia complex ion is,  $(\text{Ag}^+)(\text{NH}_4\text{OH})^2/(\text{Ag}(\text{NH}_3)_2^+) = 6 \times 10^{-8}$ .

The silver halides are soluble in excess of the halide ion to form the complex ions  $\text{AgX}_2^-$ , and  $\text{AgX}_3^{--}$  but they have not been included in the list because of the more complicated equilibria.

The potentials of a number of silver complex ions and solids as oxidizing agents are given below. The decrease in oxidizing power is, of course, due to the decrease in concentration of silver ion.

$\text{Ag} = \text{Ag}^+ + e^-$ .....	- 0.799
$2\text{Ag} + \text{SO}_4^{--} = \text{Ag}_2\text{SO}_4 + 2e^-$ .....	- 0.65
$\text{Ag} + \text{C}_2\text{H}_3\text{O}_2^- = \text{AgC}_2\text{H}_3\text{O}_2 + e^-$ .....	- 0.64
$2\text{Ag} + \text{C}_2\text{O}_4^{--} = \text{Ag}_2\text{C}_2\text{O}_4 + 2e^-$ .....	- 0.47
$2\text{Ag} + \text{CO}_3^- = \text{Ag}_2\text{CO}_3 + 2e^-$ .....	- 0.46
$\text{Ag} + \text{IO}_3^- = \text{AgIO}_3 + e^-$ .....	- 0.37
$\text{Ag} + 2\text{NH}_3 = \text{Ag}(\text{NH}_3)_2^+ + e^-$ .....	- 0.37
$2\text{Ag} + 2\text{OH}^- = \text{Ag}_2\text{O} + \text{H}_2\text{O} + 2e^-$ .....	- 0.344
$\text{Ag} + \text{Cl}^- = \text{AgCl} + e^-$ .....	- 0.222
$\text{Ag} + \text{CNS}^- = \text{AgCNS} + e^-$ .....	- 0.09
$\text{Ag} + \text{Br}^- = \text{AgBr} + e^-$ .....	- 0.07
$\text{Ag} + \text{CN}^- = \text{AgCN} + e^-$ .....	+ 0.04
$\text{Ag} + \text{I}^- = \text{AgI} + e^-$ .....	+ 0.15
$\text{Ag} + 2\text{CN}^- = \text{Ag}(\text{CN})_2^- + e^-$ .....	+ 0.29
$2\text{Ag} + \text{S}^{--} = \text{Ag}_2\text{S} + 2e^-$ .....	+ 0.71

**20. Silver Oxide.**—The brown oxide,  $\text{Ag}_2\text{O}$ , is precipitated by the addition of soluble alkalis to silver ion. The solid hydroxide is unstable and exists only momentarily. The oxide decomposes at comparatively low temperatures; the partial pressure of oxygen reaches 1 atmosphere at  $184^\circ \text{C}$ . However, the rate of decomposition does not be-



come rapid until the oxide is heated much above this temperature. The decomposition is catalyzed by metallic silver. The oxide is distinctly basic in its reactions. It reacts with as weak an acid as carbonic to form the normal **carbonate**,  $\text{Ag}_2\text{CO}_3$ . As indicated above, the oxide is soluble in a large number of reagents with the formation of complex ions. The silver ammonia hydroxide,  $\text{Ag}(\text{NH}_3)_2\text{OH}$ , is a soluble strong base. Upon standing, the alkaline solution forms a highly explosive nitride, probably  $\text{Ag}_3\text{N}$  or  $\text{Ag}_2\text{NH}$ .

**21. Silver Halides.**—Silver fluoride is extremely soluble and forms a number of hydrates. The solubility of the other halides is very slight, decreasing with increasing molecular weight. Their solubility in various reagents has been indicated above. The solubility in excess halide to form the complexes, such as  $\text{AgCl}_2^-$ , requires a fairly high concentration of the halide. The chloride and bromide are not oxidized by nitric acid, but the iodide is. The halides form a number of solid ammoniates, such as  $\text{AgCl} \cdot 3\text{NH}_3$ . Silver chloride, however, is not very soluble in liquid ammonia. The photochemical properties of the halides are discussed under the subject of photography. The chloride and bromide have the so-called “sodium chloride” arrangement of the ions in the crystal, while the iodide has two forms, one the zinc oxide and the other the zinc sulfide arrangement (Append. V). The fluoride and chloride are colorless, but the bromide is light yellow and the iodide a deeper yellow. Silver chloride may be separated from the bromide by taking advantage of the difference in solubility in ammonia. A solution containing 32 g. of ammonia and 20 g. of silver nitrate per liter will dissolve the chloride, but not appreciable amounts of the bromide.

**22. Silver Cyanide.**—Silver cyanide is precipitated by addition of cyanide, and forms the complex ion,  $\text{Ag}(\text{CN})_2^-$  or  $\text{Ag}(\text{CN})_3^{--}$ , with excess of cyanide. The role of the silver cyanide complex ion in metallurgy and silver plating has been discussed. The complex gives the smallest concentra-

tion of silver ion of any of the silver compounds except the sulfide. From the electropotential given above it is evident that, in the presence of cyanide, silver is a powerful reducing agent.

**23. Silver Nitrate.**—The nitrate is prepared commercially by the action of nitric acid upon silver. The salt is extremely soluble. Its melting point is remarkably low, about  $200^{\circ}\text{C}.$ ; cast into sticks it is used in medicine under the name of lunar caustic. At red heat, it is decomposed into metallic silver, oxygen, nitrogen, and nitrogen oxides. Many organic substances reduce it to finely divided metallic silver, as, for example, the black stains produced by the action of the salt upon the skin.

The salt is important in the preparation of other silver compounds. In dilute solutions it is used as an antiseptic, and in more concentrated solutions as a caustic. It is also used in indelible inks, especially in laundry markings.

**24. Silver Sulfide.**—The sulfide is the least soluble of all the silver salts. It is formed as a black precipitate by hydrogen sulfide, even in highly acid solutions. It is more stable toward decomposition upon heating than the oxide. Strong oxidizing agents dissolve it due to the oxidation of the sulfur. It is also somewhat soluble in concentrated cyanide ion. In the presence of air the reaction proceeds through the removal of the sulfide by oxidation to free sulfur. Metallic silver dissolves slowly in hydrogen sulfide with the evolution of hydrogen,  $2\text{Ag} + \text{H}_2\text{S} = \text{Ag}_2\text{S} + \text{H}_2$ , in accord with the large positive value for the  $\text{Ag} - \text{Ag}_2\text{S}$  couple as given above.

**25. Other Silver Salts.**—In addition to those given above, the following slightly soluble compounds may be mentioned: the **phosphate**,  $\text{Ag}_3\text{PO}_4$ ; **arsenite**,  $\text{Ag}_3\text{AsO}_3$ ; **arsenate**,  $\text{Ag}_3\text{AsO}_4$ ; **ferricyanide**,  $\text{Ag}_3\text{Fe}(\text{CN})_6$ ; and **dichromate**,  $\text{Ag}_2\text{-Cr}_2\text{O}_7$ . **Silver nitrite**,  $\text{AgNO}_2$ , is but moderately soluble, and upon standing in contact with the solution decomposes according to the equation:  $2\text{AgNO}_2 = \text{Ag} + \text{Ag}^+ + \text{NO}_3^-$

+ NO. The reaction is reversible. Silver ion also forms **alums**, such as  $\text{AgAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

**26. Photography.**—The silver halides, as well as the cyanide, show marked changes when exposed to light, especially that of the violet region of the spectrum. There is a change in color; white silver chloride, for example, becomes a deep greyish blue, and is decomposed into silver and the halogen. Many investigators have claimed the formation of **subhalides**, such as  $\text{Ag}_2\text{Cl}$  or  $\text{Ag}_4\text{Cl}_3$ , but it seems more probable that the action of the light is to cause an electron of the halide ion to pass more or less completely back to the silver without at first disrupting the crystal lattice of the ions. The result is essentially a solid solution of silver and atomic halogen in the halide, which, upon further exposure, slowly decomposes with evolution of the halogen. The halide which has been thus “activated” by light is acted upon much more readily by reducing agents than is the unexposed halide.

These photochemical reactions are the basis of the ordinary photographic processes. These may be divided into the following steps: preparation of the plate or film, exposure, development and fixation of the negative, and preparation of the positive, or print.

Dry plates or films are prepared by coating glass or celluloid with a colloidal suspension of silver bromide or chloride in gelatine. The operation must, of course, be carried out in the dark or in faint red light. The size of the particles of the silver halide affects the sensitivity of the plate to light; hence the suspension is warmed and allowed to “ripen” until the desired size of the grains is acquired.

The plate or film is exposed by projecting upon it momentarily an illuminated image. It is then developed by placing in a bath containing a reducing agent (various phenols, such as pyrogallol, metol, and hydroquinone are usually employed). The rapidity of reduction of the silver

halide is proportional to the intensity of illumination falling upon it; and as a result the image on the plate is the "negative" of the original in that the bright portions are represented by heavy deposits of silver and the dark portions by faint deposits. The action of the reducing agent is stopped when the proper contrast is obtained, and the plate "fixed" by dissolving out the unreduced silver halide with sodium thiosulfate solution ("hypo").

The process of printing is essentially the same as making the negative, but since the sensitized paper is illuminated through the negative, the image is again reversed, and now appears with the light and dark portions corresponding to the original. On the slower papers silver chloride suspension in albumen is used, while the faster papers employ silver bromide in gelatine. The print may be toned by treating with solutions of sodium chloraurate,  $\text{NaAuCl}_4$ , or potassium chlorplatinite,  $\text{K}_2\text{PtCl}_4$ , which replace the precipitated silver by gold or by platinum. The former gives a red tone, and the latter dark grey.

"Orthochromatic" and "panchromatic" plates, more sensitive to the red, yellow, and green light, are prepared by adding to the gelatine various dyes, which absorb these longer wave lengths and thus utilize their energy for the activation of the silver halide.

**27. The + 2 and + 3 Oxidation States.**—Ozone acts upon solutions of  $\text{Ag}^+$  forming  $\text{AgO}^+$  and  $\text{Ag}^{++}$ , probably by the following steps:



At equilibrium the ratio of  $\text{Ag}^{++}/\text{AgO}^+$  is quite large. The solutions are highly unstable as the ions oxidize water readily with the evolution of  $\text{O}_2$ . Powerful oxidizing agents in alkaline solution form  $\text{AgO}$  and  $\text{Ag}_2\text{O}_3$ . The approximate values for the standard potentials are:

	VOLTS <sub>25°</sub>
$\text{Ag}^+ = \text{Ag}^{++} + e^-$ .....	- 1.98
$\text{Ag}^{++} + \text{H}_2\text{O} = \text{AgO}^+ + 2\text{H}^+ + e^-$ .....	ca - 2.1
$2\text{OH}^- + \text{Ag}_2\text{O} = 2\text{AgO} + \text{H}_2\text{O} + 2e^-$ .....	- 0.57
$2\text{OH}^- + 2\text{AgO} = \text{Ag}_2\text{O}_3 + \text{H}_2\text{O} + 2e^-$ .....	- 0.74

**28. Analytical.**—Silver is detected by the precipitation of the chloride, insoluble in nitric acid, but soluble in ammonium hydroxide. It may be distinguished from the slightly soluble lead and mercurous chlorides by the fact that the former is soluble in hot water, but not in ammonia, while the latter turns black with ammonia. Silver is determined gravimetrically by precipitating and weighing as the chloride, bromide, or as the metal precipitated electrolytically. Silver may be titrated volumetrically with a solution of thiocyanate. Ferric ion is used as an indicator, since the deep red ferric thiocyanate is less stable than the silver salt, and the red color appears only when the silver has been almost completely precipitated. Silver is also titrated in dilute nitric acid with a standardized solution of alkali chloride or bromide, by taking advantage of the coagulation and settling of the precipitate with sufficient rapidity to permit the observation of any precipitate produced by further addition of the halide.

## GOLD

**29. Occurrence.**—Gold is found in nature as the free metal, as the telluride,  $\text{AuTe}_2$ , and also as complex tellurides, e.g.  $\text{AuAgTe}_4$ . The sulfide, selenide, or chloride do not occur. Sea water contains gold to the extent of 0.01 to 0.3 part per million. The name reef gold is given to the deposits of gold occurring in quartz veins. Upon the weathering of the auriferous rocks, the gold has been washed into sand and gravel beds to form alluvial or placer deposits. Native gold nearly always contains silver and the platinum metals.

**30. Metallurgy.**—The richer deposits of gold have been worked for centuries by methods which recovered only the larger particles of the metal and which could not be applied to low grade ores. The crude methods of placer mining have been the simple agitation or washing of the gravel with water to bring about a separation of the heavy gold particles from the lighter materials. The use of mercury as an aid in the process by the amalgamation of the metal was probably introduced as early as 500 B.C.

The modern metallurgy of gold is quite similar to that of silver. Gold in copper and lead ores is recovered, along with the silver, by methods already discussed. The separation of the gold from the silver is known as "parting," and is usually carried out either by electrolytic methods or by the use of solvents, such as concentrated sulfuric or nitric acids, which dissolve the silver by oxidation, but not the gold. In the former case the impure metal is made the anode, with a solution of chlorauric acid as electrolyte. Pure gold deposits on the cathode. Silver is precipitated as the chloride together with the platinum metals in the anode mud. If excess silver is present, the electrolyte may be silver nitrate solution, in which case gold remains as sludge at the anode and silver deposited on the cathode.

The introduction of the cyanide process by Macarthur and Forest about 1890 has contributed enormously to the world's gold supply through rendering available for commercial treatment low grade ores and also "tailings" from the amalgam process. The potential of the half reaction,  $\text{Au} + 2\text{CN}^- = \text{Au}(\text{CN})_2^- + e^-$ , is about + 0.6 volt, that is, the gold in the presence of cyanide is a good reducing agent; hence by treating gold ore with a dilute cyanide solution in the presence of air, the metal is easily oxidized by the oxygen:  $4\text{Au} + 8\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{Au}(\text{CN})_2^- + 4\text{OH}^-$ . Hydrogen peroxide appears to be formed as an intermediate step (cf. III—4). The reaction is not rapid and requires a number of days. The gold is precipitated from



the solution by zinc or by electrolysis. High grade ores, after being pulverized in a mill, may first be washed over amalgamated copper plates to remove the larger gold particles which do not dissolve rapidly in the cyanide. The amalgam is scraped off the plates, and the gold recovered by distillation of the mercury.

**31. The Metal.**—The more important physical properties are given in Table I. Gold is the most malleable and ductile of all metals. It may be rolled into sheets 0.00001 mm. thick and drawn into wire which weighs but 0.0005 g. per meter. The world's yearly production is about 1,000 tons. The gold used in jewelry is alloyed with copper. The copper alloys are redder, harder, and more fusible than pure gold. The temperature-composition curves for the alloy show a minimum melting point at 890° C. with a composition of 82 per cent gold. The purity of the metal is usually expressed in carats, that is, the number of parts of gold in 24 parts of the metal. The best jewelry is 15 to 18 carat gold. American coinage is 21.6 carat (90 per cent). Gold is deposited in electroplating from a solution of aurocyanide, and much cheap jewelry is manufactured by so depositing a very thin coat of gold on copper.

Gold is easily obtained in the **colloidal state**, especially in the presence of other stabilizing colloids. Thus, **purple of Cassius** is finely divided gold adsorbed on a hydrosol of stannic acid. The gold colloids may be formed by reduction of gold solution with chemical agents, or by electrical dispersion, using an arc between gold electrodes under water.

TABLE VI  
REACTIONS OF METALLIC GOLD

$2\text{Au} + 3\text{Cl}_2 = 2\text{AuCl}_3$	At about 150°; also with $\text{Br}_2$
$\text{Au} + 2\text{Te} = \text{AuTe}_2$	
$\text{Au} + 6\text{H}_2\text{SeO}_4 = \text{Au}_2(\text{SeO}_4)_3 + 3\text{SeO}_2 + 6\text{H}_2\text{O}$	
$\text{Au} + 5\text{H}^+ + 4\text{Cl}^- + \text{NO}_3^- = \text{HAuCl}_4 + \text{NO} + 2\text{H}_2\text{O}$	Solution in aqua regia
$2\text{Au} + 4\text{CN}^- + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = 2\text{Au}(\text{CN})_2^- + 2\text{OH}^-$	
$2\text{Au} + 2\text{Na}_2\text{S}_3 = 2\text{NaAuS}_2 + \text{Na}_2\text{S}_2$	
$2\text{Au} + \text{I}_2 = 2\text{AuI}$	

**32. Equilibria between Oxidation States.**—Aurous ion is unstable in respect to the decomposition:  $6\text{Au}^+ + 3\text{H}_2\text{O} = 4\text{Au} + \text{Au}_2\text{O}_3 + 6\text{H}^+$  (about 0.3 volt); hence only those aurous compounds and complexes which are relatively less soluble and less ionized than the corresponding auric compound can be prepared in solution. The only aurous compound which appears to be really stable with respect to the auric in solution is the aurocyanide:  $\text{Au}(\text{CN})_4^- + 2\text{Au} + 2\text{CN}^- = 3\text{Au}(\text{CN})_2^-$ .

Oxidation reduction potentials are summarized in Table VII. The value given for the formation of aurocyanide, + 0.6 volt, may be too high, as gold does not appear to dissolve in cyanide solution with the evolution of hydrogen.

TABLE VII  
OXIDATION REDUCTION POTENTIALS OF GOLD

$\text{Au} = \text{Au}^+ + e^-$ .....	ca - 1.68
$\text{Au}^+ = \text{Au}^{+++} + 2e^-$ .....	ca - 1.29
$\text{Au} + 2\text{CN}^- = \text{Au}(\text{CN})_2^- + e^-$ .....	+ 0.6
$\text{Au} + 2\text{Br}^- = \text{AuBr}_2^- + e^-$ .....	0.96
$2\text{Br}^- + \text{AuBr}_2^- = \text{AuBr}_4^- + 2e^-$ .....	- 0.82
$\text{Au} + 4\text{Cl}^- = \text{AuCl}_4^- + 3e^-$ .....	- 1.0
$\text{Au} + 4\text{OH}^- = \text{AuO}_2^- + 2\text{H}_2\text{O} + 3e^-$ .....	ca - 0.5

Auric chloride and bromide decompose upon heating to give the aurous halide:  $\text{AuCl}_3 = \text{AuCl} + \text{Cl}_2$ . Many of the auric compounds, however, decompose, giving the metal. A number of + 2 compounds also exist, but they are all unstable with respect to the reaction,  $3\text{Au}^{++} = \text{Au} + 2\text{Au}^{+++}$ , with the exception of the sulfide  $\text{AuS}$ . Like mercuric sulfide this gold sulfide is very slightly soluble and may be precipitated from a solution of auric chloride.

**33. Oxides.**—The aurous oxide,  $\text{Au}_2\text{O}$ , is said to be formed by the action of dilute potassium hydroxide upon aurous chloride, but it is very unstable and, in excess hydroxide, gives the metal and aurate,  $\text{AuO}_2^-$ . The addition of hydroxide to auric solutions gives a precipitate of  $\text{Au}(\text{OH})_3$ , or more probably the hydrous sesquioxide,  $\text{Au}_2\text{O}_3$ . This is amphoteric, and is somewhat more acidic than basic. The

alkali aurates, such as  $\text{KAuO}_2$ , are soluble; but those of the alkaline earths are not. The oxide forms with ammonia the highly explosive gold "**fulminate**," probably  $\text{AuN}\cdot\text{NH}_3$ . An unstable + 2 oxide,  $\text{AuO}$ , is also known.

**34. Halides.**—Fluorine does not attack gold at ordinary temperatures, but at higher temperatures a slight reaction occurs. The fluoride is completely hydrolyzed by water, forming auric hydroxide. Chlorine attacks gold in the neighborhood of  $150^\circ$ , forming  $\text{AuCl}_3$ . At somewhat higher temperatures the aurous chloride,  $\text{AuCl}$ , is formed. This is but slightly soluble in water. Both chlorides are soluble in excess hydrochloric acid, forming, respectively,  $\text{HAuCl}_4$  and  $\text{HAuCl}_2$ . The latter is unstable, as discussed above. Auric chloride is usually prepared by the action of **aqua regia** upon gold. Sodium chloraurate,  $\text{NaAuCl}_4\cdot 2\text{H}_2\text{O}$ , is employed in photography in toning prints. The two bromides,  $\text{AuBr}$  and  $\text{AuBr}_3$ , are analogous in most respects to the chlorides. Gold is slowly attacked by iodine, forming  $\text{AuI}$ . However, there appears to be a measurable equilibrium:  $2\text{Au} + \text{I}_2 = 2\text{AuI}$ . The aurous iodide is also formed by the reaction:  $\text{Au}_2\text{O}_3 + 6\text{HI} = 2\text{AuI} + 3\text{H}_2\text{O} + 2\text{I}_2$ , or by the addition of iodide to the auric chloride. Auric iodide is unstable.

**35. Sulfides.**—Gold and sulfur do not unite when heated together, but gold is dissolved by molten alkali polysulfides, forming thioaurites and possibly some thioaurates. Hydrogen sulfide in warm acid solution gives with  $\text{AuCl}_4^-$  a precipitate of gold and sulfur. In cold solution some of the unstable sulfide,  $\text{AuS}$ , appears to be formed.

**36. Other Compounds.**—Mention has been made of the occurrence of gold **telluride**, and also of the stability and importance of the **cyanoaurites**. The alkali cyanoaurites, such as  $\text{KAu}(\text{CN})_2$ , are soluble. Auric nitrate and sulfate are so highly hydrolyzed that auric oxide is soluble only in very concentrated solution of these acids.

**37. Analytical.**—The presence of auric gold may be determined by the rose coloration (colloidal gold) produced

upon the addition of a dilute solution of stannous chloride to the auric solution in excess hydrochloric acid. Gold, in the form of auric chloride, is sometimes determined quantitatively by the reaction,  $\text{AuCl}_4^- + 3\text{I}^- = \text{AuI} + \text{I}_2 + 4\text{Cl}^-$ , the liberated iodine being titrated with thiosulfate (cf. **X—20**). Gold ores are usually analyzed by the fire assay. The first step in the assay is the separation of the gangue, and the concentration of gold and silver in a lead "button." This operation may be carried out in a shallow clay dish called a "scorifier," in which the sample of ore is heated with a large amount of lead and a little borax. Much of the lead is oxidized, and the oxide forms an easily fusible flux with the silicates and borates. The rest of the lead serves to collect the gold and silver, and when the molten mass is cooled the lead is found as a small lump or button which may be separated from the slag. This process is sometimes carried out in a crucible with a mixture of ore, fluxing agent, lead oxide, and some reducing agent. The latter reduces some of the lead oxide, and the metal collects the gold and silver as in the scorification process. The second step is the separation of the gold and silver from the lead. The button is heated in a little cup of bone ash called a "cupel." The lead oxidizes, and the liquid oxide is readily absorbed by the bone ash, while the liquid gold and silver remain in a small globule. The third step is the "parting" of the gold and silver. The button is flattened by hammering and treated with nitric acid to dissolve out the silver. Unless there is a considerable excess of silver, more must be added before the separation can be accomplished, as otherwise the silver atoms are removed from the surface of the button but the crystal lattice is not destroyed, and the action soon stops. However, if there is a large excess of silver, the crystal is completely disintegrated, and the finely divided gold remaining may be fused and weighed. Gold is readily separated from the platinum metals by precipitation with hydroquinone in 1.2*N* HCl solutions.

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## Chapter VIII

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### SUBGROUP II. ZINC, CADMIUM, AND MERCURY

1. The elements of Subgroup II, zinc, Zn, cadmium, Cd, and mercury, Hg (hydrargyrum), differ from the elements of the main group in much the same way that copper, silver, and gold differ from the alkali metals. Thus the subgroup elements are more noble, their hydroxides are less basic, and their ions have a greater tendency to form complex ions. These properties depend upon the much higher ionization potentials of the atoms and the smaller size of the resultant ions (Table I). The melting points of the elements in Subgroup II are much lower than those of the main group. They all form + 2 positive ions, but in addition, mercury forms an unusual series of compounds of the ion,  $\text{Hg}_2^{++}$ , and cadmium appears to form the + 1 chloride and oxide. These elements are less noble than the corresponding elements of Subgroup I, and their hydroxides are more acidic.

Zinc and cadmium resemble each other much more closely than they do mercury. They are distinctly electropositive, are readily oxidized by hydrogen ion, and their oxides are reduced with difficulty; while mercury is a noble metal, and its oxide is easily decomposed upon simple heating. The solubility of the oxide in water increases with increasing size of the metal ion. Zinc oxide is amphoteric, dissolving readily in both acids and bases. Cadmium and mercuric oxides dissolve in acids, and unstable cadmates and mercurates are

also known. Both zinc and cadmium form stable hydroxides, but mercury does not. Mercuric salts are very highly hydrolyzed, notwithstanding the appreciable solubility of mercuric oxide. One of the outstanding characteristics of the subgroup is the slight dissociation of the chlorides, bromides, and iodides. This property is most pronounced with the mercuric ion. In the most stable salts and complexes, the apparent ionic radii are 10 or 15 per cent less than the values given in Table I, as the high attractive force is able to distort the ions from their normal shapes (cf. VII—2).

TABLE I

ATOMIC AND PHYSICAL PROPERTIES OF ZINC, CADMIUM, AND MERCURY

	Zn	Cd	Hg
Atomic number . . . . .	30	48	80
Atomic weight . . . . .	65.38	112.41	200.61
Isotopes . . . . .	64, 66, 67, 68, 70	106, 108, 110, 111, 112, 113, 114, 116	196, 197, 198, 199, 200, 201, 202, 204
Electrons in various quantum levels, 1st . . . . .	2	2	2
2d . . . . .	8	8	8
3d . . . . .	18	18	18
4th . . . . .	2	18	32
5th . . . . .		2	18
6th . . . . .			2
Radius of $M^{++}$ in crystals $\times 10^8$ cm. . . . .	0.74	0.97	1.10
Ionization potential of gase- ous atoms in volts,			
1st electron . . . . .	9.36	8.96	10.38
2d electron . . . . .	17.89	16.84	18.65
Melting point $^{\circ}$ C. . . . .	419.4	320.9	— 38.87
Boiling point $^{\circ}$ C. . . . .	907	767	356.9
Density of solids . . . . .	7.14	8.6	14.19 at — 40 $^{\circ}$
Electrical resistance ohm-cm. $\times 10^6$ . . . . .	6	7.5 at 20 $^{\circ}$	21.3 at — 50 $^{\circ}$
Potential of electrode: M = $M^{++} + 2e^{-}$ in volts . .	+ 0.762	+ 0.402	— 0.854
Solubility of $Zn(OH)_2$ , $Cd(OH)_2$ , and $HgO$ , g. per liter . . . . .	$2.6 \times 10^{-6}$	$2.6 \times 10^{-4}$	$5 \times 10^{-3}$



## ZINC AND CADMIUM

**2. Occurrence.**—The principal zinc ores are the sulfide,  $\text{ZnS}$ , called sphalerite or zinc blende; and the carbonate,  $\text{ZnCO}_3$ , smithsonite. Other ores are: willemite,  $\text{Zn}_2\text{SiO}_4$ ; calamine,  $\text{Zn}_2(\text{OH})_2\text{SiO}_3$ ; zincite,  $\text{ZnO}$ ; and franklinite,  $[\text{Fe}, \text{Zn}, \text{Mn}](\text{FeO}_2)_2$ . The average percentage of zinc present in igneous rocks is estimated as  $4 \times 10^{-5}$ .

Most zinc ores contain some cadmium. The average ratio of zinc to cadmium is about 200 to 1. The yellow cadmium sulfide sometimes occurs fairly pure and is known as greenockite.

**3. Metallurgy.**—The major portion of the zinc ore is smelted by reduction with carbon, although more than a hundred thousand tons of pure zinc are now produced yearly by a process which combines the extraction of the ore by leaching, and the electrolytic reduction of the metal from the solution. In the former process the ore is first crushed and concentrated by washing out the lighter rocks, or, in the case of the sulfide, by "flotation" methods (see Metallurgy of Lead). Sulfide and carbonate ores are roasted to convert them into the oxide:  $2\text{ZnS} + 3\text{O}_2 = 2\text{ZnO} + 2\text{SO}_2$ . Much of the sulfur dioxide liberated is recovered and made into sulfuric acid. The oxide is mixed with coal, and the mixture heated in small clay retorts (4 to 5 feet long). A temperature of 1,200 to 1,300° C. is required for reduction, and as the boiling point of the metal is only 907°, the metal is vaporized as soon as it is liberated:  $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$ . A sufficient excess of coal is employed to prevent the formation of carbon dioxide, since zinc is oxidized by the dioxide. A small condenser is placed over the mouth of the retort, and its temperature is controlled so as to condense the metal to the liquid state. If the temperature of the condenser is below the melting point of the zinc, the metal collects in the form of a fine powder called zinc dust, which also contains a small per cent of zinc

oxide. Even under the best conditions, some zinc dust is formed, and 10 per cent or even more of the zinc escapes from the condenser along with the carbon monoxide. The liquid is drawn off and cast into molds, forming what is known as "spelter." It usually contains, as the principal impurities, a per cent or so of lead and smaller amounts of iron and cadmium. The metal may be purified by distillation in vacuum or in hydrogen, but it is difficult to effect a complete separation from the lead.

In the electrolytic process sulfide ore is first carefully roasted at a low temperature, and under these conditions forms largely sulfate. The ore is then leached with dilute sulfuric acid, and the acid sulfate solution treated with a small quantity of zinc dust to precipitate the nobler metals, as these would deposit along with the zinc upon electrolysis of the solution. Although the potential required to precipitate zinc is 0.762 volt greater than the reversible reduction potential for hydrogen ion, the overvoltage of hydrogen on pure zinc is sufficiently great (1.23 volts in 1*N* H<sup>+</sup>) to permit the deposition of zinc in acid solution if a high cathodic current density is used. Electrolytic zinc is very pure, and commands a higher price for that reason. The annual production of zinc is over a million tons.

Cadmium is both more easily reduced and more volatile than zinc; consequently, it is concentrated in the first portions of the distillate in zinc smelting, and may be recovered from the zinc by fractional distillation. However, most of the commercial product now comes from the electrolytic zinc process, the cadmium being precipitated along with the more noble metals in the purification of the electrolyte.

**4. The Metals.**—The more important physical properties have been summarized in Table I. Zinc takes a good white metallic luster upon polishing, but the surface quickly tarnishes to the familiar blue-grey tinge. Zinc is hard and brittle at ordinary temperatures, but between 100° and 150° it becomes malleable enough to permit rolling and

drawing. At somewhat higher temperatures, it becomes so brittle that it may be pulverized in a mortar. These changes appear to be due to allotropic forms, but the transitions from one form to another have not been definitely determined.

Zinc is used in making brass (see Copper) and many other alloys. It is used in dry cells (see Manganese) and the preparation of zinc pigments (see Oxide, Sulfate, and Sulfide). The largest use of the metal, however, is in galvanizing iron. The process is carried out in three different ways: (1) dipping the iron into molten zinc, (2) depositing the zinc upon the iron by electrolytic reduction, (3) exposing the iron to the action of zinc vapor, called "sherardizing." Galvanized iron resists the action of weather better than pure iron, largely due to the impervious coating of basic zinc carbonate on the surface, but in part to the fact that the electropositive character of the zinc tends to prevent a hole wearing through the iron by furnishing electrons in place of the iron. Zinc dust is employed as a reducing agent in the manufacture of dyes.

Cadmium has a silver white color with a slight bluish tinge. It is not as hard as zinc, and at ordinary temperatures is much more ductile and malleable. Like zinc, however, it becomes very brittle at higher temperatures, the change likewise appearing to be due to a crystalline transition. The electrical conductivity of cadmium is somewhat less than that of zinc.

Cadmium is used as a substitute for tin in antifriction metals and solders, its principal use being in bearing metals for automobiles. Its presence in small amounts in copper wire adds strength with but small reduction in the conductivity. Cadmium plating is now used to rust-proof wires, tools, and other iron and steel articles. After plating, the articles are heat-treated, thus alloying the cadmium and iron. Corrosion tests indicate that cadmium plate and zinc plate have about the same resistance.

**5. Reactions of the Metals.**—Zinc dust is subject to spontaneous combustion in moist air, but in more compact forms does not burn readily until heated above 500° C. Pure zinc is almost insoluble in dilute hydrogen ion, due to the very large overvoltage of the hydrogen. If, however, the metal be touched with some metal with a low overvoltage for hydrogen, such as nickel or platinum, the evolution of hydrogen takes place rapidly on the surface of the other metal, and the zinc dissolves. The high positive value of the oxidation-reduction potential (Table I) renders it possible to dissolve zinc by a number of oxidizing agents. The metal is soluble in rather concentrated alkali with the evolution of hydrogen and formation of zincate. These and other reactions are summarized in Table II.

TABLE II  
REACTIONS OF ZINC METAL

$2\text{Zn} + \text{O}_2 = 2\text{ZnO}$	Upon heating
$\text{Zn} + 2\text{H}^+ = \text{Zn}^{++} + \text{H}_2$	Slow with pure zinc
$\text{Zn} + 2\text{H}_2\text{O} = \text{Zn}(\text{OH})_2 + \text{H}_2$	With steam at high temperature
$\text{Zn} + \text{OH}^- + \text{H}_2\text{O} = \text{HZnO}_2^- + \text{H}_2$	With concentrated alkali
$\text{Zn} + \text{S} = \text{ZnS}$	Also with Se, Te, P, As, etc.
$\text{Zn} + \text{X}_2 = \text{ZnX}_2$	X is any halogen
$\text{Zn} = \text{Zn}^{++} + 2e^-$	0.762 volt
$\text{Zn} + \text{CO}_2 = \text{ZnO} + \text{CO}$	At red heat
$4\text{Zn} + 2\text{O}_2 + 3\text{H}_2\text{O} + \text{CO}_2 = \text{Zn}_4\text{CO}_3(\text{OH})_6$	The protective coating on zinc surfaces

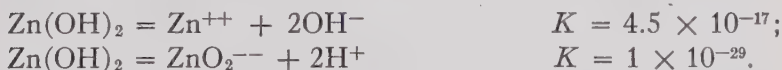
The reactions of cadmium are, in general, similar to those of zinc, but the lower positive value of the oxidation reduction couple, 0.402 volt, renders it considerably less reactive with oxidizing agents. Unlike zinc, it does not dissolve in alkali.

**6. Zinc and Cadmium Ions.**—The ions  $\text{Zn}^{++}$  and  $\text{Cd}^{++}$  are colorless and poisonous to most organisms, cadmium more so than zinc. Zinc ion is rather highly hydrolyzed, while cadmium ion is only slightly so. Zinc ion forms as its more important slightly soluble compounds:  $\text{Zn}(\text{OH})_2$ ,  $\text{ZnCO}_3 \cdot n\text{Zn}(\text{OH})_2$ ,  $\text{ZnNH}_4\text{PO}_4$ ,  $\text{Zn}_3(\text{PO}_4)_2$ ,  $\text{ZnP}_2\text{O}_7$ ,  $\text{ZnC}_2\text{O}_4$ ,

$\text{Zn}(\text{CN})_2$ ,  $\text{Zn}(\text{IO}_4)_2$ ,  $\text{Zn}_2\text{Fe}(\text{CN})_6$ , and  $\text{ZnS}$ . Its most stable complex ions are  $\text{Zn}(\text{NH}_3)_4^{++}$ ,  $\text{Zn}(\text{CN})_4^{--}$ , and  $\text{HZnO}_2^-$ . Cadmium ion forms the precipitates:  $\text{Cd}(\text{OH})_2$ ,  $\text{CdCO}_3$ ,  $\cdot n\text{Cd}(\text{OH})_2$ ,  $\text{Cd}(\text{CN})_2$ ,  $\text{Cd}_2\text{Fe}(\text{CN})_6$ , and  $\text{CdS}$ ; and the complex ions,  $\text{Cd}(\text{NH}_3)_4^{++}$ ,  $\text{Cd}(\text{CN})_4^{--}$ , and  $\text{CdI}_4^{--}$ .

**7. Oxides and Hydroxides.**—Zinc oxide,  $\text{ZnO}$ , occurs as the mineral zincite. It is an important commercial commodity, and is prepared by the oxidation of the metal or directly from the oxidized ores by heating a mixture of carbon and ore in an air blast. The carbon reduces the oxide, but the zinc vapor is immediately reoxidized, and the oxide carried along as a fine dust in the flue gas, from which it is finally recovered by the use of filter bags. This oxide is used extensively as a white pigment, generally mixed with white lead. It is employed in the manufacture of automobile tires, and in medicine as a base for various ointments. It may be formed by gently heating the hydroxide, but it will not combine with water to form the hydroxide. It is yellow when hot, and white when cold. The arrangement of the zinc and oxide ions in the crystal lattice is given in Appendix V.

The hydroxide is precipitated upon the addition of hydroxide ion to a solution of zinc ion. It is amphoteric, and readily soluble in excess hydroxide and in acids:



The solid zincates, such as  $\text{K}_2\text{ZnO}_2$ , are prepared by fusion of the two oxides, but are highly hydrolyzed in solution. Zinc hydroxide is soluble in ammonium hydroxide, due to the stability of the complex,  $\text{Zn}(\text{NH}_3)_4^{++}$ . The value for the dissociation constant of the complex is  $K = 9.8 \times 10^{-10}$ . Peroxides in alkaline solution form with zinc salts the hydrated zinc peroxide,  $\text{ZnO}_2 \cdot 2\text{H}_2\text{O}$ .

The brown cadmium oxide,  $\text{CdO}$ , is formed by methods similar to those discussed for zinc oxide. Cadmium hy-



droxide, (solubility product,  $1.2 \times 10^{-14}$ ), is more soluble and more basic than zinc hydroxide. It does not dissolve in excess hydroxide ion, but cadmates are said to be formed by fusing cadmium oxide in potassium hydroxide. Cadmium hydroxide is soluble in ammonium hydroxide, and cyanides with the formation of the complex ions:  $\text{Cd}(\text{NH}_3)_4^{++}$  ( $K = 2.5 \times 10^{-7}$ ), and  $\text{Cd}(\text{CN})_4^{--}$  ( $K = 1 \times 10^{-17}$ ). A hydrated cadmium peroxide similar to the zinc peroxide exists, and **cadmous hydroxide**,  $\text{Cd}_2(\text{OH})_2$ , appears to form when a base is added to the unstable cadmous chloride. The hydroxide is a powerful reducing agent.

**8. Halides.**—Although zinc and cadmium fluorides are but moderately soluble, the other halides are readily soluble. They crystallize from their solutions as hydrated salts, usually with 4 moles of water at low temperatures, and one mole at higher temperatures. Solutions of the zinc salts are distinctly acid by hydrolysis, and readily precipitate basic halides upon the addition of dilute alkali. Concentrated solutions of zinc chloride dissolve zinc oxide and set to form a cement,  $\text{ZnOHCl}$ , similar to the magnesia cement. The chloride in the fused state also dissolves metal oxides, and is much used as a flux in soft soldering.

In their concentrated solutions, the halides appear to be slightly ionized, due to the formation of complex ions. This property is exhibited somewhat by the zinc salts and markedly by the cadmium. The latter forms, for example,  $\text{CdCdCl}_4$  and  $\text{CdCdF}_4$ . The complex ion,  $\text{CdI}_4^{--}$ , is fairly stable, the value for the dissociation constant being about  $5 \times 10^{-7}$ .

**Cadmous chloride**,  $\text{Cd}_2\text{Cl}_2$ , appears to be formed by heating the dichloride and metal together at about  $800^\circ$ . It is hydrolyzed by water to  $\text{Cd}_2(\text{OH})_2$ .

**9. Sulfates.**—The crystallization of an aqueous solution of zinc sulfate at ordinary temperature forms the heptahydrate,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ; and solutions of cadmium sulfate



form the hydrate,  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ . A number of other hydrates also occur at higher and lower temperatures. These hydrates are very soluble in water. Large quantities of zinc sulfate are used in the preparation of the white pigment, **lithopone**, the reaction being:  $\text{ZnSO}_4 + \text{BaS} = \text{BaSO}_4 + \text{ZnS}$ . This pigment does not blacken with hydrogen sulfide, as does white lead, and possesses fair covering power. Cadmium sulfate is employed in the manufacture of "standard cells" for electrical measurements. These cells have an anode of cadmium amalgam, a cathode of mercurous sulfate in contact with mercury, and an electrolyte of cadmium sulfate solution.

**10. Sulfides.**—Zinc sulfide is the only common white metallic sulfide. Cadmium sulfide is yellow. Zinc sulfide is precipitated by the addition of alkali or ammonium sulfides to solutions of zinc salts. Its solubility is increased by hydrogen ion:  $\text{ZnS} + \text{H}^+ = \text{Zn}^{++} + \text{HS}^-$ ; but it may be fairly completely precipitated in a solution of acetic acid with sodium acetate added to reduce the hydrogen ion concentration. The value for the solubility product is  $4.5 \times 10^{-24}$ . Cadmium sulfide is much less soluble ( $K = 1.4 \times 10^{-28}$ ), and may be precipitated from highly acid solutions. Neither sulfide is soluble in excess of sulfide ion, but both are slightly soluble in high concentrations of ammonium hydroxide, due to the formation of the complex ammonia ions. Cadmium sulfide is also soluble in iodide, as mentioned under the halides, but it is not soluble in cyanide. Cadmium sulfide is an excellent yellow pigment, but is too expensive for extensive application.

**11. Other Salts.**—The **nitrates** are readily prepared by dissolving the metals or oxides in nitric acid. Normal **zinc carbonate** exists in nature, and may be precipitated from zinc solution with sodium bicarbonate, but basic carbonates are precipitated from solution by the alkali carbonates. Cadmium shows less tendency to form basic carbonates than does zinc. Basic zinc phosphate, made from the oxide

and phosphoric acid, is important as a cement in dentistry. See also Appendix XIX.

**12. Analytical.**—The separation of zinc and cadmium from other metallic elements is indicated in the standard scheme of analysis (Append. VI). The separation of aluminum from zinc, by the precipitation of aluminum hydroxide with excess ammonium hydroxide, carries down considerable zinc as zinc aluminate, and, for this reason, in detecting small amounts of zinc, it is preferable to precipitate the aluminum as  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , by adding ether and hydrogen chloride gas. The insolubility of cadmium sulfide in excess sulfide ion distinguishes it from arsenic, antimony, and tin; and its solubility in hot nitric acid gives a separation from mercuric sulfide. The precipitation of cadmium sulfide in the presence of cyanide ions serves to distinguish cadmium from copper.

Zinc may be determined quantitatively by precipitating as the sulfide, igniting, and weighing as the oxide; by precipitation as  $\text{ZnNH}_4\text{PO}_4$ , and weighing as  $\text{Zn}_2\text{P}_2\text{O}_7$ ; or by precipitation by cathodic reduction from an acetic acid-acetate buffer solution. In the electrolytic determination, it is difficult to obtain a complete precipitation of the metal. The most satisfactory volumetric method is the titration of zinc with ferrocyanide. The formation of a brown color with an uranyl solution as an outside indicator is used to determine the end-point, or a few drops of ferrous ion may be added to the zinc solution, in which case the color changes from light blue to pea-green at the end-point. This latter color change appears to be due to the presence of a trace of ferricyanide, which gives a blue color until an excess of ferrocyanide is obtained.

Cadmium may be determined gravimetrically by precipitating as carbonate and weighing as oxide; or, similarly to zinc, precipitating as phosphate and weighing as  $\text{Cd}_2\text{P}_2\text{O}_7$ . It is impossible to precipitate the sulfide pure enough to weigh as such, as it forms complexes, e.g.,  $\text{Cd}_2\text{Cl}_2\text{S}$ . Cad-

mium may also be determined electrolytically by reduction from a solution of the cyanide complex.

## MERCURY

**13. Occurrence.**—Mercury occurs native and in amalgams of gold and silver, but the principal ore is cinnabar,  $\text{HgS}$ . Complex selenides, tellurides, and chlorides also occur, but they are of slight economic importance. The average percentage of mercury in the igneous rocks is estimated as  $10^{-7}$ .

**14. Metallurgy.**—The extraction of mercury from the sulfide ore is comparatively simple, since the sulfide may readily be converted into the volatile metal, either by roasting in air:  $\text{HgS} + \text{O}_2 = \text{Hg} + \text{SO}_2$ ; or by roasting with lime:  $4\text{HgS} + 4\text{CaO} = 3\text{CaS} + \text{CaSO}_4 + 4\text{Hg}$ . The mercury vapor is more easily condensed from the furnace gases than is zinc, because of the greater weight of the molecules of vapor, and also because the vapor is not readily reoxidized by air. The metal is filtered through chamois skin and purified by washing with nitric acid, or mercurous nitrate solution; or by distillation in the presence of oxygen, or other oxidizing agents, which will remove the base metals, especially zinc and cadmium.

**15. The Metal.**—The more important physical properties have been given in Table I. The metal is a silvery-white liquid with a vapor pressure of 0.001 mm. at  $20^\circ$  and 0.28 mm. at  $100^\circ$ . Its boiling point is  $356.90^\circ$ . A table of densities of the liquid is given in Appendix IX. The vapor is monatomic, and does not conduct electricity in the cold, but if an arc is once struck it conducts readily with the emission of the characteristic mercury spectrum which is very rich in green and ultra-violet light. This mercury vapor arc is much used as a current rectifier, and as a source of ultra-violet light for the treatment of certain diseases. The cubical coefficient of expansion of mercury between  $0^\circ$

and  $300^{\circ}$  is represented by the expression:  $\alpha = 1.8006 \times 10^{-4} + 2 \times 10^{-8}t$ . Due to this rather uniform expansion and to the fact that the pure liquid does not "wet" glass, mercury is extensively used in thermometers. Its low vapor pressure and high density makes it useful in barometers. With the exception of iron and platinum, metals readily dissolve in, or are wet by mercury to form amalgams; many of these have been mentioned in connection with other metals, e.g. sodium, aluminum, gold, and silver. An amalgam of thallium (8.5 per cent Tl) has a very low melting point and may be used in thermometers down to  $-60^{\circ}\text{C}$ . Amalgams of tin, silver, gold, and other metals are employed in dentistry. Many attempts have been made to use mercury in heat engines, as the higher boiling point offers a very substantial increase in the theoretical efficiency over the steam engine, and two plants are now in operation in the United States. These installations employ 300,000 pounds of mercury.

TABLE III  
REACTIONS OF THE METAL

$2\text{Hg} + \text{O}_2 = 2\text{HgO}$	Slowly around $350^{\circ}$
$\text{Hg} + \text{X}_2 = \text{HgX}_2$	X is any halogen
$\text{Hg} + \text{S} = \text{HgS}$	Upon subliming together
$3\text{Hg} + 2\text{NO}_3^- + 8\text{H}^+ = 3\text{Hg}^{++} + 2\text{NO} + 4\text{H}_2\text{O}$	Excess acid
$6\text{Hg} + 2\text{NO}_3^- + 8\text{H}^+ = 3\text{Hg}_2^{++} + 2\text{NO} + 4\text{H}_2\text{O}$	Excess mercury
$\text{Hg} + \text{SO}_4^{--} + 4\text{H}^+ = \text{Hg}^{++} + \text{SO}_2 + 2\text{H}_2\text{O}$	Hot concentrated acid

**16. Equilibria between Oxidation States.**—The mercurous ion is stable in respect to the decomposition into mercuric ion and mercury: i.e., mercuric ion is reduced by mercury:  $\text{Hg}^{++} + \text{Hg} = \text{Hg}_2^{++}$ . However, the value for the potential of the reaction corresponds to an equilibrium concentration of  $\text{Hg}_2^{++}$  at  $25^{\circ}\text{C}$ ., only 81 times that of  $\text{Hg}^{++}$ ; hence the equilibrium is easily reversed in case the mercuric compound is much less soluble than the mercurous: e.g.,  $\text{Hg}_2\text{S} = \text{HgS} + \text{Hg}$  and  $\text{Hg}_2\text{O} = \text{HgO} + \text{Hg}$ . Due to the insolubility of the basic ammonia mercuric salts (Par. 25), all mercurous compounds are decomposed by

ammonia. The equilibrium lies in the direction of the mercuric form at higher temperatures. In this respect the higher oxidation state is different from copper, since cupric oxide upon heating gives cuprous oxide and oxygen, while mercuric oxide gives mercury and oxygen. Mercuric sulfate, however, decomposes at high temperatures according to the equation:  $2\text{HgSO}_4 = \text{Hg}_2\text{SO}_4 + \text{SO}_2 + \text{O}_2$ .

The couple  $\text{Hg}^{++}\text{-Hg}^+$  is a stronger oxidizing couple than  $\text{Hg}^{++}\text{-Hg}$  (Table IV); hence reducing agents first reduce mercuric ion to mercurous. Since the potential of the couple  $\text{Hg}^+\text{-Hg}$  is almost as large, most reducing agents capable of reducing mercuric ion will, in excess, reduce the mercurous ion to mercury as a second step: e.g.,  $2\text{Hg}^{++} + \text{Sn}^{++} = 2\text{Hg}^+ + \text{Sn}^{++++}$ , and  $2\text{Hg}^+ + \text{Sn}^{++} = 2\text{Hg} + \text{Sn}^{++++}$ . It also follows from the potential values that fairly powerful oxidizing agents, e.g., bromine water and hot nitric acid, are required to oxidize mercurous compounds to mercuric, unless, of course, the mercuric compound is much less soluble or less ionized.

TABLE IV

## OXIDATION-REDUCTION POTENTIALS OF MERCURY

	VOLTS <sub>25°</sub>
$\text{Hg} + \text{S}^{--} = \text{HgS} + 2e^-$ .....	+ 0.70
$\text{Hg} + 4\text{CN}^- = \text{Hg}(\text{CN})_4^{--} + 2e^-$ .....	+ 0.37
$\text{Hg} + 4\text{I}^- = \text{HgI}_4^{--} + 2e^-$ .....	+ 0.04
$2\text{Hg} + 2\text{I}^- = \text{Hg}_2\text{I}_2 + 2e^-$ .....	+ 0.04
$\text{Hg} + 2\text{OH}^- = \text{HgO} + \text{H}_2\text{O} + 2e^-$ .....	- 0.098
$2\text{Hg} + 2\text{Br}^- = \text{Hg}_2\text{Br}_2 + 2e^-$ .....	- 0.14
$2\text{Hg} + 2\text{SCN}^- = \text{Hg}_2(\text{SCN})_2 + 2e^-$ .....	- 0.22
$2\text{Hg} + 2\text{Cl}^- = \text{Hg}_2\text{Cl}_2 + 2e^-$ .....	- 0.2675
$2\text{Hg} + \text{CO}_3^{--} = \text{Hg}_2\text{CO}_3 + 2e^-$ .....	- 0.32
$2\text{Hg} + \text{C}_2\text{O}_4^{--} = \text{Hg}_2\text{C}_2\text{O}_4 + 2e^-$ .....	- 0.41
$2\text{Hg} + \text{SO}_4^{--} = \text{Hg}_2\text{SO}_4 + 2e^-$ .....	- 0.615
$2\text{Hg} = \text{Hg}_2^{++} + 2e^-$ .....	- 0.799
$\text{Hg} = \text{Hg}^{++} + 2e^-$ .....	- 0.854
$\text{Hg}_2^{++} = 2\text{Hg}^{++} + 2e^-$ .....	- 0.910
$\text{HgS} = \text{S} + \text{Hg}^{++} + 2e^-$ .....	- 1.05

## MERCUROUS COMPOUNDS

**17. Mercurous ion** is strikingly similar to silver ion in the solubility of its salts, and in the potential of reduction to the



metal. However, the mercurous ion is peculiar in that it is associated into the double ion,  $\text{Hg}_2^{++}$ , not only in solution, but in its compounds in the solid and gaseous state. Indeed it is somewhat doubtful if the undissociated ion  $\text{Hg}^+$  exists. From the standpoint of atomic structure, the mercurous ion is quite unusual. The variations in the oxidation states of the Subgroup I elements arises through the possibility of removing electrons from the kernel, but the mercurous ion consists of the kernel plus one valence electron. Many examples may be given of the association of molecules containing an odd number of electrons; and the formation of  $(\text{Hg} : \text{Hg})^{++}$  may be correlated with this general behavior of "odd" molecules. The mercurous ion does not form complex ions with the ammonia, cyanide, iodide, or thio-sulfate, as does silver ion.

**18. Mercurous oxide**,  $\text{Hg}_2\text{O}$ , is formed by the action of alkalis upon soluble mercurous salts. It is not soluble in excess hydroxide ion. The oxide decomposes slowly at  $25^\circ$ , and rapidly at  $100^\circ$ , into mercury and mercuric oxide. The speed of decomposition is increased by light.

**19. Mercurous chloride**,  $\text{Hg}_2\text{Cl}_2$ , or calomel, is the most important mercurous salt. It is usually prepared by subliming a mixture of mercuric chloride and mercury:  $\text{HgCl}_2 + \text{Hg} = \text{Hg}_2\text{Cl}_2$ . It is formed as a white precipitate by the addition of chloride to a solution of mercurous nitrate. Mercurous chloride sublimes without melting, and if dry, the vapor consists of  $\text{Hg}_2\text{Cl}_2$  molecules, but moisture catalyzes its decomposition into mercury and mercuric chloride. Light causes a partial decomposition of the salt at room temperature. Mercurous chloride turns dark when treated with ammonia, due to the formation of finely divided mercury and the ammonio-basic mercuric chloride (Par. 25). The use of calomel in medicine depends upon its stimulating action upon the liver and other secretive organs. The potential of the reaction:  $2\text{Hg} + 2\text{Cl}^- = \text{Hg}_2\text{Cl}_2 + 2e^-$  is  $-0.2675$  volt (i.e., molal chloride ion activity and referred



to the potential of hydrogen arbitrarily chosen as zero); and the electrode: mercury—solid mercurous chloride—chloride ion, is often employed as a reference electrode in potential measurements. The potential of the electrode changes slightly in air. Thus with 1M KCl the values are  $-0.2825$  in air and  $-0.2812$  in absence of air. Much work has been done on the absolute value of this electrode potential, and the value 0.56 volt is usually accepted; the mercury is positive with respect to the solution.

**20. Mercurous fluoride, bromide, and iodide** resemble the corresponding silver salts in respect to solubility in water. The iodide is unstable, especially with excess iodide, and decomposes into mercury and mercuric iodide.

**21. Mercurous sulfide** may be formed momentarily by the action of hydrogen sulfide upon mercurous salts, but it immediately decomposes into mercury and mercuric sulfide. **Mercurous nitrate** and **sulfate** may be prepared by the action of nitric acid and of hot concentrated sulfuric acid, respectively, upon excess mercury. The nitrate is readily soluble, but the sulfate only sparingly so. Both are hydrolyzed, and unless excess acid is present, form slightly soluble basic salts, such as  $\text{Hg}_2(\text{OH})\text{NO}_3$  and  $\text{Hg}_2\text{OHg}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ .

**Mercurous phosphate, nitrite, chromate, bromate, and iodate**, are but slightly soluble. Alkali carbonates precipitate **mercurous carbonate** from soluble mercurous salts. The carbonate is unstable if warmed slightly:  $\text{Hg}_2\text{CO}_3 = \text{Hg} + \text{HgO} + \text{CO}_2$ . **Mercurous cyanide** is not stable.

#### MERCURIC COMPOUNDS

**22. Mercuric oxide**,  $\text{HgO}$ , is slowly formed as a red powder when mercury is heated in air just below its boiling point. It is usually prepared by heating the nitrate or a mixture of the nitrate and mercury:  $\text{Hg}(\text{NO}_3)_2 + \text{Hg} = 2\text{HgO} + 2\text{NO}_2$ . The partial pressure of oxygen over mercuric oxide is 985 mm. at  $500^\circ \text{C}$ . The oxide precipitates

upon the addition of a strong base to a solution of a mercuric salt. Precipitated in the cold, the color is yellow, but from hot solutions, the color is red. The difference in color seems to be merely a question of the state of subdivision of the solid, as the two forms appear to have the same crystal structure and very nearly the same energy content. The yellow is the more reactive and also the more finely divided. The hydroxide is unstable, but a hydrate,  $\text{HgO} \cdot 3\text{H}_2\text{O}$ , exists. The oxide is soluble in excess iodide due to the formation of the complex iodide:  $\text{HgO} + 4\text{I}^- + \text{H}_2\text{O} = \text{HgI}_4^{--} + 2\text{OH}^-$ . Its solubility increases slightly in alkali, due to weak acidic properties and the formation of  $\text{HHgO}_2^-$ .



Mercuric ion in solution is more highly hydrolyzed than is to be expected from the value for the solubility of the oxide, Table I. However, the value for the oxide electrode:  $\text{Hg} + 2\text{OH}^- = \text{HgO} + \text{H}_2\text{O} + 2e^-$ ,  $-0.098$  volt, indicates that the concentration of  $\text{Hg}^{++}$  in the solution is very small.

**23. Mercuric chloride**,  $\text{HgCl}_2$ , "bichloride of mercury" or "corrosive sublimate," may be made by heating mercury in an atmosphere of chlorine. The reaction is accompanied by green radiation. It is usually prepared, however, by subliming a mixture of mercuric sulfate and common salt. The chloride is moderately soluble in water, and the solubility is increased by excess chloride ion due to the formation of complex ions, probably  $\text{HgCl}_4^{--}$ . The salt in solution is but slightly ionized, even less than cadmium chloride, as is indicated by its low electrical conductivity, and by the value of the chloride as an oxidizing agent:  $\text{Hg}_2\text{Cl}_2 + 2\text{Cl}^- = 2\text{HgCl}_2 + 2e^-$ ,  $-0.62$  volt. This value is 0.3 volt lower than the  $\text{Hg}_2^{++}$ - $\text{Hg}^{++}$  couple in spite of the small solubility of the mercurous chloride. The solution is only slightly hydrolyzed, but the addition of dilute alkali results in the formation of various basic chlorides, such as  $\text{HgCl}_2 \cdot \text{HgO}$ . The chloride is much used as an antiseptic and is highly

poisonous. It forms a slightly soluble compound with albumen, and advantage is taken of this fact in administering egg white as an antidote. As a poison it acts partly through the destruction of kidney cells to such an extent that death results in about two weeks from the inability of the body to eliminate its waste products. The commercial preparation is usually mixed with sodium chloride to increase the rate of solution.

**24. Mercuric fluoride** is more soluble and much more hydrolyzed than the chloride. The **bromide** is sparingly soluble, and the **iodide** still less soluble. The iodide exists in two modifications, a scarlet form stable below  $128^{\circ}$ , and a yellow form stable above that temperature. The yellow iodide may be super-cooled below the transition temperature, but readily changes to the scarlet when touched. Mercuric iodide dissolves in excess iodide forming the very stable complex iodide,  $\text{HgI}_4^{--}$ . A solution of the potassium complex iodide is known as **Nessler's reagent**, and is used in detecting small amounts of ammonia (see below).

**25. Mercuric ammonia compounds** exist in interesting variety, divisible into four types: (1) Soluble complexes giving the ion  $\text{Hg}(\text{NH}_3)_4^{++}$ . This ion is stable only at very high (12*N*) concentrations of  $\text{NH}_4\text{OH}$ ; (2) with ammonia of crystallization, such as  $\text{HgCl}_2 \cdot 2\text{NH}_3$ ; (3) basic salts of the ammonia system, that is, they are formed from the negative ions of ammonia,  $\text{NH}_2^-$ ,  $\text{NH}^{--}$ , and  $\text{N}^{---}$ , similar to negative ions of water  $\text{OH}^-$  and  $\text{O}^{--}$ , the simplest being of the type  $\text{HgNH}_2\text{Cl}$ ; (4) salts which are both ammonolyzed and hydrolyzed. Many complex salts of this latter type exist. The most important are derivatives of Millon's base,  $\text{OHHgNHHgOH}$ , or  $\text{Hg}_2\text{NOH} \cdot \text{H}_2\text{O}$ . The addition of ammonium hydroxide to mercuric chloride solution precipitates the ammonobasic chloride,  $\text{HgNH}_2\text{Cl}$ . With mercurous chloride, the same compound mixed with mercury is formed. The ammonobasic chloride is soluble in hydrochlo-

ric acid and dissolves more readily if some ammonium ion is present. Ammonia and mercuric nitrate solution form  $\text{Hg}_2\text{N}\cdot\text{NO}_3$  and a number of other complex salts. Nessler's reagent (Par. 24) gives, with ammonia, a yellow precipitate, the iodide of Millon's base,  $\text{Hg}_2\text{NI}\cdot\text{H}_2\text{O}$ .

**26. Mercuric Sulfide.**—Crystalline mercuric sulfide is red, both as found in nature, cinnabar, and as prepared by subliming together mercury and sulfur; but the sulfide precipitated from solution by hydrogen sulfide is black and amorphous. The black form is transformed slowly into the red by digestion with sodium sulfide. Mercuric sulfide is the least soluble ( $K = 3 \times 10^{-53}$ ) of all the metal sulfides, and does not dissolve in hydrochloric or nitric acids. It is, however, soluble in aqua regia and in bromine water, due to the stability of the complex halides. Hot concentrated nitric acid converts it into the difficultly soluble white complex,  $\text{Hg}(\text{NO}_3)_2\cdot 2\text{HgS}$ . The sulfide has weak acidic properties, and is somewhat soluble in a solution of an alkali sulfide but not in ammonium sulfide. The red sulfide is used as a pigment under the name of vermilion.

**27. Mercuric nitrate and sulfate** are formed by the action of excess nitric and hot concentrated sulfuric acids upon the metal. Both are soluble, but are rather highly hydrolyzed, and precipitate as basic salts, such as  $\text{Hg}(\text{NO}_3)_2\cdot\text{HgO}$  and  $\text{HgSO}_4\cdot 2\text{HgO}$ , unless excess acid is present. Normal mercuric carbonate does not exist, but **basic carbonates**, such as  $\text{HgCO}_3\cdot 2\text{HgO}$ , may be precipitated. **Mercuric cyanide**,  $\text{Hg}(\text{CN})_2$ , is soluble, but is even less ionized than the halides, and like them forms a complex ion,  $\text{Hg}(\text{CN})_4^{--}$ . When heated, it decomposes into mercury and cyanogen:  $\text{Hg}(\text{CN})_2 = \text{Hg} + \text{C}_2\text{N}_2$ . This complex gives the smallest concentration of mercuric ion of any of the mercuric compounds except the sulfides.

**Mercuric fulminate**,  $\text{Hg}(\text{CNO})_2$ , is formed by the addition of alcohol to a hot solution of mercury in nitric acid. The dry precipitate explodes upon being struck, and is used

extensively in percussion caps. **Mercuric thiocyanate**,  $\text{Hg}(\text{CNS})_2$ , is slightly soluble. "Pharaoh's serpents" are prepared from this salt by making it into a paste with gum-water. When dried and ignited it burns and forms a voluminous ash which assumes serpentine forms.

**28. Analytical.**—Mercurous ion, like silver, gives a curdy, white precipitate with chloride but, unlike silver chloride, the precipitate blackens with ammonia (Par. 25). The insolubility of mercuric sulfide in nitric acid and in ammonium polysulfide serves to identify mercuric ion. The addition of stannous chloride to mercuric ion in small amounts gives a white precipitate of mercurous chloride, and in excess, a grey precipitate of mercury. With mercurous ion, stannous chloride in small amounts gives an immediate precipitate of mercury. A copper wire in either mercurous or mercuric solutions becomes coated with a grey or silvery deposit of mercury.

Mercury may be precipitated and weighed quantitatively as the sulfide, or electrolytically as the metal on a platinum cathode. It is sometimes determined by heating the sample in a combustion tube and passing the vapors through a weighing tube containing gold leaf to absorb the mercury. Mercurous salts may be precipitated and weighed as the chloride. Mercuric salts are sometimes analyzed volumetrically by titration with iodide.

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# Chapter IX

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## SUBGROUP III. GALLIUM, INDIUM, AND THALLIUM

1. The elements of Subgroup III are extremely rare and of slight industrial importance. They form compounds in which they have an oxidation state of + 3, and, in the case of thallium, compounds also of the + 1 state. In spite of the higher positive charge on their ions, they do not show as great tendencies to form "coordination compounds" or complexes as do the elements of Subgroup II. The first electron is rather easily removed, and as a consequence, compounds of the elements give characteristic colors in hot Bunsen flames; in fact, all of the elements of this group were discovered (between 1860–1875) through spectroscopic means. The name thallium (from Latin *thallus*, a budding twig) refers to its green spectrum; and the name indium, to its indigo-blue spectral lines. Gallium was named in honor of France (Latin, *Gallia*).

The + 3 compounds are similar to those of aluminum; with the exception that the acid character of the hydroxides decreases with increasing size of the atoms, and the potential of the ions as oxidizing agents increases.

2. **Occurrence.**—The elements occur widely distributed, but only in minute quantities. The average percentages of the elements present in igneous rocks are given as: gallium,  $10^{-11}$ ; indium,  $10^{-11}$ ; and thallium,  $10^{-10}$ . Gallium is a common constituent of zinc, iron, aluminum, and chromium ores, but is seldom present in quantities as high as 0.01 per



cent. In small amounts, it is a very common impurity in pig iron and in commercial aluminum. Indium is usually associated with zinc blende, and often with ores of tungsten and tin. Its principal source is zinc, in which it sometimes occurs to the extent of 0.1 per cent. It is estimated that several thousand tons of gallium and indium could be recovered yearly as by-products of the zinc and coal industries. Thallium is associated with the alkalies, and also with iron, zinc, lead, tellurium, and other elements. It is most commonly obtained from the flue dust of sulfuric acid works in which thalliferous pyrites are burned.

**3. Preparation of Metals.**—The extraction of the metals is largely a problem of separating the small quantities of their compounds from other metallic constituents, and is, therefore, best considered after a discussion of the properties of the various ions. The metals are easily obtained by reduction with zinc, or by electrolysis.

TABLE I  
ATOMIC AND PHYSICAL PROPERTIES

ELEMENT	GALLIUM	INDIUM	THALLIUM
Symbol.....	Ga	In	Tl
Atomic weight.....	69.72	114.76	204.39
Atomic number.....	31	49	81
Isotopes.....	69, 71	113, 115	203, 205
Ionization potential of gaseous atoms in volts, 1st electron.....	5.97	5.76	6.07
2d electron.....	20.43	18.79	20.32
3d electron.....	30.6	27.9	29.7
Radius of ion in crystals, cm. $\times 10^8$ ...	0.62	0.81	0.95 (ic) 1.15 (ous)
Melting point ° C.....	29.75	155	303.5
Boiling point ° C.....	1,700	> 1,450	1,650
Density.....	5.91	7.3	11.85
Electrical resistivity, ohm/cm. $\times 10^6$ ..	53 at 0°	9 at 20°	18.1 at 20°
Electrode potential, M = M <sub>(aq.)</sub> <sup>+++</sup> + 3e <sup>-</sup> volts.....	+ 0.52	+ 0.34	- 0.72
Principal spectral lines, wave lengths, cm. $\times 10^8$ .....	4,172.2 4,033.2	4,511.55 4,101.95 3,256.22 3,039.46	3,519.37 3,775.89 5,350.70

**4. The Metals.**—Many of the properties of the metals have been summarized in Table I. **Gallium** is a hard, brittle, grey metal. It melts just above room temperature, and remains a silver white liquid of low vapor pressure through a temperature range of about 1,500 degrees. The metal expands upon changing from liquid to solid. The liquid supercools readily and may be kept in the liquid state even at  $0^{\circ}\text{C}$ . A possible application is in the construction of high temperature thermometers using quartz tubes. **Indium** is a lustrous silver metal almost as soft as lead, and is both ductile and malleable. Its commercial applications are very limited at present. Suggested uses include the manufacture of a non-tarnishing silver alloy, and as a protective coating for automobile bearings. **Thallium** is bluish-white in color, easily cut with a knife, malleable, but of low tensile strength. The metal exists in two crystalline modifications with a transition at  $226^{\circ}\text{C}$ . Like the other two metals, the liquid is stable over a very long range of temperature.

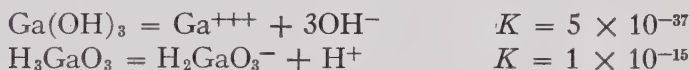
**5. Reactions of the Metals.**—Gallium is only superficially oxidized in air at red heat; indium is not appreciably oxidized in air at  $25^{\circ}$ , but burns with a blue flame when heated, forming  $\text{In}_2\text{O}_3$ ; thallium oxidizes slowly at  $25^{\circ}$ , and rapidly at higher temperatures, forming both  $\text{Tl}_2\text{O}$  and  $\text{Tl}_2\text{O}_3$ . Gallium and indium dissolve fairly readily in hydrogen ion with the evolution of hydrogen gas and the formation of the ions; thallium dissolves forming thalious ion or thalious salts. They unite directly with the more electronegative elements, and are, of course, oxidized by even moderately strong oxidizing agents, as indicated by their oxidation-reduction potentials (Table I).

**6. Gallic Ion and Its Compounds.**—Gallic ion is colorless and its salts with colorless negative ions are white. Gallic oxide,  $\text{Ga}_2\text{O}_3$ , resembles aluminum oxide. Gallous oxide,  $\text{Ga}_2\text{O}$ , is known but it is unstable with respect to its decomposition into the + 3 oxide and the metal. The **hydroxide**,  $\text{Ga}(\text{OH})_3$ , is precipitated by alkali and ammonium

TABLE II  
REACTIONS OF THE METALS

$4M + 3O_2 = 2M_2O_3$	Ga slowly. Tl also forms $Tl_2O$
$2M + 6H^+ = 2M^{+++} + 3H_2$	With Ga and In. Tl forms $Tl^+$
$2M + 2OH^- + 2H_2O = 2MO_2^- + 3H_2$	With Ga
$2M + 3X_2 = 2MX_3$	X denotes halogens. Tl also forms TlX
$2M + 3S = M_2S_3$	Analogous reactions with Se, Te, P, As.

hydroxides, and the precipitate is soluble in excess of the reagent, forming **gallates**. Approximate values for the basic and acidic dissociation constants are:



Gallic ion, like aluminum, in the presence of carbonate ion, is completely hydrolyzed, leading to the precipitation of the hydroxide. The **sulfates**, **nitrates**, and **halides** are soluble, but the solutions are highly hydrolyzed and precipitate basic salts upon boiling. A **dichloride**,  $GaCl_2$ , appears to be formed by heating the trichloride with excess of the metal. The salt evolves hydrogen in water and forms basic gallic chloride. Gallic ion readily forms **alums**. The **ferrocyanide** is insoluble, even in solutions strongly acid with hydrochloric acid. The white **sulfide**,  $Ga_2S_3$ , is not precipitated except in the presence of other sulfides, such as zinc, copper, or arsenic, and then only when the solution is alkaline or but slightly acid.

**7. Analytical.**—Gallium is precipitated with the iron aluminum zinc group in qualitative analysis. It may be separated from the other elements of the group, except ferric iron, by converting to the chloride and extracting with an ether-hydrogen chloride solution. The iron may be removed by reduction to ferrous and repeating the ether separation. The commercial separation from the zinc, with which it is usually associated, may be effected by converting

into the chlorides, and fractional precipitation by sodium carbonate. The gallium concentrates in the first precipitate. It is separated from indium by taking advantage of the greater solubility of gallium hydroxide in excess alkali. The separation from zinc and indium may also be accomplished by fractional electrolytic precipitation. Quantitatively gallium is precipitated with aqua ammonia, removing the excess ammonia by boiling, and is weighed as the sesquioxide.

**8. Indic Ion and Compounds.**—The ion,  $\text{In}^{+++}$ , is colorless; ammonia or alkali hydroxides precipitate it as the **hydroxide**,  $\text{In}(\text{OH})_3$ . The hydroxide forms the **sesquioxide**,  $\text{In}_2\text{O}_3$ , upon heating, and upon strong ignition the oxide,  $\text{In}_3\text{O}_4$ . Heated to  $300^\circ$  in hydrogen, the oxide,  $\text{In}_2\text{O}_2$ , appears to be formed. The hydroxide is soluble to a very small extent in strong alkali hydroxide (but not in dilute ammonium hydroxide), probably forming **indate** ion,  $\text{InO}_2^-$ . The carbonate is but slightly soluble, and, unlike gallium, is but slightly hydrolyzed. It is soluble in excess ammonium carbonate, but not in excess sodium carbonate. The **nitrate**, **sulfate**, **alums**, and **halides** are soluble. The halides resemble the cadmium compounds in that they are weak salts. **Mono-** and **dihalides** are formed by heating the trichlorides with excess metal, but these lower halides are unstable in water solutions:  $3\text{In}^+ = \text{In}^{+++} + 2\text{In}$ , and  $3\text{In}^{++} = 2\text{In}^{+++} + \text{In}$ . From analogy to mercurous ion the  $+2$  ion should have the formula  $\text{In}_2^{+4}$ . Yellow indium **sulfide**,  $\text{In}_2\text{S}_3$ , is precipitated by hydrogen sulfide in the presence of very dilute acid. It is somewhat soluble in a very high concentration of sulfide ion. The **cyanide** is but slightly soluble in water, but dissolves in excess cyanide. The **ferrocyanide** and **chromate** are also but slightly soluble.

**9. Analytical.**—The separation of indium from indiferous zinc, the principal source of the element, is usually accomplished by dissolving the metal in acid, and precipitating indium and iron by the addition of ammonium hydroxide.

The indium is separated from the iron present by dissolving the hydroxides and precipitating indium sulfide in acetic acid solution by hydrogen sulfide.

In the systematic qualitative separation, indium, like gallium, is precipitated with the iron-aluminum-zinc group. It is similar to zirconium and titanium in that the hydroxide is not dissolved when boiled with NaOH and Na<sub>2</sub>O<sub>2</sub>, but differs in the precipitation of the sulfide from a fluoride solution by NH<sub>4</sub>OH and (NH<sub>4</sub>)<sub>2</sub>S.

**10. Equilibria between Thallous and Thallie Ions.**—Thallie ion, Tl<sup>+++</sup>, is a strong oxidizing agent (Table III), being reduced to thallous ion, Tl<sup>+</sup>. Further reduction requires a fairly powerful reducing agent. The reaction, Tl<sup>+++</sup> + 2Tl = 3Tl<sup>+</sup>, takes place practically to completion. Hot water is decomposed by thallie ion: Tl<sup>+++</sup> + H<sub>2</sub>O = Tl<sup>+</sup> + 2H<sup>+</sup> +  $\frac{1}{2}$ O<sub>2</sub>. Thallie compounds decompose in general, upon heating, with the formation of the thallous compound: e.g. TlCl<sub>3</sub> = TlCl + Cl<sub>2</sub>, and Tl<sub>2</sub>S<sub>3</sub> = Tl<sub>2</sub>S + 2S.

TABLE III  
OXIDATION-REDUCTION POTENTIALS OF THALLIUM

	VOLTS
Tl + I <sup>-</sup> = TlI + e <sup>-</sup> .....	0.77
Tl + Br <sup>-</sup> = TlBr + e <sup>-</sup> .....	0.66
Tl + Cl <sup>-</sup> = TlCl + e <sup>-</sup> .....	0.56
Tl = Tl <sup>+</sup> + e <sup>-</sup> .....	0.336
Tl <sup>+</sup> = Tl <sup>+++</sup> + 2e <sup>-</sup> .....	- 1.2

**11. Thallous Ion and Compounds.**—In the solubilities of most of its salts, thallous ion resembles plumbous ion; while in size and other physical properties, basic nature of the hydroxide, and lack of tendency to form complex ions, it resembles potassium. Thallous ion is like stannous and plumbous ions in having a pair of valence electrons left in the valence energy level. **Thallous oxide**, Tl<sub>2</sub>O, readily absorbs water to form **thallous hydroxide**, TlOH. The latter is fairly soluble and is a strong base. The decomposition pressure of steam over the hydroxide, 2TlOH = Tl<sub>2</sub>O



+  $\text{H}_2\text{O}$ , reaches one atmosphere at  $139^\circ \text{C}$ . The **chloride**, **bromide**, and **iodide** are but sparingly soluble, and the solubility is decreased by the presence of excess halide ion. However, the **cyanide** appears to be soluble in excess cyanide ion. **Thallous sulfide**,  $\text{Tl}_2\text{S}$ , is precipitated in neutral or alkaline solution. The solubility product of the sulfide is given as  $1.2 \times 10^{-24}$ . **Thallous carbonate** is fairly soluble. The **chromate**, normal **phosphate**, **chloroplatinate**, and **cobaltinitrite** are sparingly soluble. Thallous sulfate is sometimes used in the preparation of poison grain to kill rodents.

**12. Thallic Ion and Its Compounds.**—Thallic ion resembles aluminum ion except that it is larger, and its **hydroxide** does not possess acid properties. The hydroxide is extremely insoluble and the soluble thallic compounds such as **sulfate** and **nitrate** are highly hydrolyzed. Oxygen reacts with thallium just below red heat to form thallic oxide,  $\text{Tl}_2\text{O}_3$ ; at higher temperatures mixed thallic and thallous oxides are formed. Chlorine, passed into a suspension of thallous chloride, produces **thallic chloride**. Upon evaporation, the hydrate,  $\text{TlCl}_3 \cdot 3\text{H}_2\text{O}$ , may be obtained, and in the presence of ammonia the ammoniate,  $\text{TlCl}_3 \cdot 3\text{NH}_3$ , separates. The trichloride forms complex ions with excess chloride, and a complex **thallous chlorthallate** exists,  $\text{TlTlCl}_4$ . The **bromide** is quite similar to the chloride, but the **iodide**,  $\text{TlI}_3$ , is probably thallous triiodide. The **sulfide**,  $\text{Tl}_2\text{S}_3$ , is very unstable, and forms thallous sulfide and sulfur.

**13. Analytical.**—Thallous chloride is soluble in hot water and not in ammonia, thus resembling lead chloride. The iodide is much less soluble than the chloride and is considered the most satisfactory test for thallous ion. It is but slightly soluble in thiosulfate. The extraction of thallium from the flue dust of sulfuric acid plants is based upon the slight solubility of the chloride, the non-precipitation of thallous carbonate by alkali carbonates, the precipitation of thallous sulfide by ammonium sulfide, and the reduction of



the compounds to the metal by zinc. Quantitatively, thallium is usually precipitated and weighed as the thallos iodide. It may also be determined by titrating with standard permanganate, which in acid solution oxidizes thallos salts to thallic.

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# Chapter X

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## GROUP VII. THE HALOGENS: FLUORINE, CHLORINE, BROMINE, IODINE

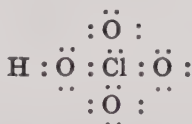
1. The elements of Group VII, fluorine, F, chlorine Cl, bromine, Br, iodine, I, are called the halogens from a Greek word meaning salt-producing, since they all combine with the alkali metals to produce salts like sodium chloride. Fluorine and chlorine are gases; bromine is a volatile liquid; and iodine is a solid, easily melted and vaporized. The chemical behavior of these elements is related to the fact that each has 7 valence electrons (Table I). The removal of one of the 7 valence electrons requires a rather high potential, as shown by the value of the ionization potential of the gaseous atoms. This group tends to add an extra electron so as to produce the octet of the noble gas element of next higher atomic number (Chap. II). With increasing size of the atoms, i.e., going down the periodic group, the attraction for the electrons decreases, as is shown by the decreasing ionization potential and electron affinity. Because of their high electron affinity the halogens are powerful oxidizing agents,  $X_2 + 2e^- = 2X^-$ , although much of the energy of the reaction in water arises from the energy of hydration of the negative ion. Fluorine not only has the largest electron affinity, but, due likewise to its small size, the ion has the highest energy of hydration; consequently fluorine is the most powerful oxidizing agent the chemist can prepare.

These elements, with the exception of fluorine, also give

compounds in which their oxidation state is positive, as illustrated by the following:

	HClO	HClO <sub>2</sub>	HClO <sub>3</sub>	HClO <sub>4</sub>
Oxidation state . . . . .	+1	+3	+5	+7

It is arbitrary to assume that the halogen has lost electrons to the oxygen in such compounds, for the electrons are probably in reality shared by both, as indicated by the electron formulas, such as

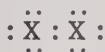


From this picture, it is obviously untrue that the actual charge upon the chlorine atom is +7. The concept of the oxidation state of +7 is most useful in correlating oxidation and reduction reactions. The *half reaction* which relates chlorine and perchlorate in aqueous acid solutions is,



Thus the oxidation of the element to perchlorate involves the loss of seven electrons. Actually this loss is shared between the chlorine and the oxygen but for simplicity we ascribe all of it to the chlorine and say the oxidation state is +7.

The tendency to form an octet with the valence electrons is made evident in the free element by the formation of the diatomic molecules in which the 2 atoms share their 7th electrons, so that each is in at least partial possession of an octet.



As might be expected, the bond grows weaker with increasing atomic radius, as shown by the increasing ease of dis-

sociation, and also by the decreased constraint under which the shared electrons are held, which is evident from the increasing dielectric constant.

TABLE I  
PROPERTIES OF THE HALOGENS

NAME	FLUORINE	CHLORINE	BROMINE	IODINE
Symbol.....	F	Cl	Br	I
Melting point ° C.....	-223	-102.1	-7.3	113
Boiling point ° C.....	-188.3	-34.7	58.0	183
Color of gas.....	Light yellow	Greenish yellow	Reddish brown	Violet
Atomic volume of solid, cc.....	17.15	23.52	27.13	34.23
Atomic weight.....	19.0	35.46	79.92	126.92
Isotopes.....	19	35, 37	79, 81	127
Atomic number.....	9	17	35	53
Electrons in various quantum levels, 1st.....	2	2	2	2
2d.....	7	8	8	8
3d.....	—	7	18	18
4th.....	—	—	7	18
5th.....	—	—	—	7
Ionizing potential of gaseous atoms, volts.....	17.34	12.95	11.80	10.6
Electron affinity of gaseous atoms, volts.....	4.13	3.75	3.53	3.22
Radius of $X^-$ in crystals, cm. $\times 10^8$ .....	1.36	1.81	1.95	2.16
Heat of vaporization, cal. per mole.....	1,640	4,420	7,418	10,388
Heat of fusion, cal. per mole.....	—	1,615	2,580	3,650
Reaction } { Heat, cal. per mole.....	62,600	56,900	45,200	35,400
$X_2 = 2X$ } { Dissoc. constant at 1000°.....	—	$10^{-8}$	0.008	0.1
Dielectric constant of solid.....	—	2.0	3.2	4.0
Solubility in water, moles of $X_2$ per liter, 20°.....	Decomposes	0.090 (1 atm.)	Liq. 0.210	Sol. 0.00133
Distribution ratio, solubility $CCl_4/H_2O$ , 0°.....	—	20.0	27.0	85.5

**2. Occurrence.**—The estimated per cent of the halogens in the earth's crust is: F, 0.1; Cl, 0.2; Br, 0.001; I, 0.001. Sea water contains about 2 per cent of chloride ion, and 0.006 per cent of bromide ion. The greater portion of the fluorine is in the form of fluorspar,  $CaF_2$ , and cryolite,  $Na_3AlF_6$ . The occurrence of great deposits of the alkali halides is discussed under the alkali elements. In addition to the alkali halides, there are found in nature chlorides, bromides, and iodides of the alkaline earths, silver, lead, copper, mercury, and bismuth. The major portion of the bromine of commerce formerly came from the bromo-

carnallite,  $\text{MgBr}_2 \cdot \text{KBr} 6\text{H}_2\text{O}$ , of the Stassfurt (Germany) deposits, and from various American salt brines, especially those of the Saginaw Valley, Michigan. With the introduction of the modern method for the extraction of bromine from sea water, this source now supplies most of the American market. The principal source of iodine is the Chile deposits, where it occurs largely in the form of iodate,  $\text{NaIO}_3$ , and periodate,  $\text{NaIO}_4$ . The largest source in the United States is from the oil well brines in California. Blood contains approximately 0.25 per cent chlorine as chloride ion, and the gastric juices 0.2 to 0.4 per cent free hydrochloric acid. Iodine is found in the various human tissues, the thyroid gland containing the highest per cent. Many marine plants exercise a selective absorption of iodide, even in the presence of far greater concentrations of chloride and bromide; hence dried seaweed is another important source of iodine.

**3. Preparation and Uses of Free Elements.—Fluorine** was first prepared by Moissan (1886) by the electrolysis of potassium fluoride in liquid hydrogen fluoride in a platinum vessel. It is now more conveniently prepared by the electrolysis of fused sodium or potassium hydrogen fluoride, using a copper vessel and graphite anode. Copper is attacked by fluorine, but the surface layer of copper fluoride protects the vessel from corrosion.

**Chlorine.** Although the greenish yellow fumes formed by the oxidation of chlorides by various oxidizing agents had long been observed, it remained for Scheele (1774) to clear up their meaning. He prepared chlorine by heating a mixture of manganese dioxide and hydrochloric acid. He considered the gas to be "dephlogisticated muriatic acid," meaning muriatic acid (hydrochloric) freed from phlogiston (the element of combustion).

Davy (1810) established its identity as an element. Scheele's method is still the one usually used for its laboratory preparation. It is also prepared by dropping dilute

hydrochloric acid upon potassium permanganate:  $2\text{KMnO}_4 + 16\text{HCl} = 8\text{H}_2\text{O} + 2\text{KCl} + 2\text{MnCl}_2 + 5\text{Cl}_2$ , and by the action of dilute sulfuric acid upon bleaching powder:  $\text{CaCl}(\text{ClO}) + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + \text{H}_2\text{O} + \text{Cl}_2$ .

Most of the chlorine of commerce is prepared by the electrolysis of brine as described under the preparation of sodium hydroxide. The annual production in the United States is over 400,000 tons. From the equilibrium electrode potentials (Append. II), one would expect oxygen to be liberated upon electrolysis of a brine solution; and this is the case in low concentration of salt:  $0.2N$   $\text{NaCl}$  yields about 20 per cent oxygen and 80 per cent chlorine at the anode. However, the oxygen evolution requires a high overvoltage (Append. I), and in more concentrated solutions only 1 or 2 per cent of oxygen is liberated.

The Deacon process, employing the oxidation of hydrogen chloride by oxygen (Par. 5), has been of some importance in the past. Attempts have also been made to operate the reaction,  $\text{MgCl}_2 + \frac{1}{2}\text{O}_2 = \text{MgO} + \text{Cl}_2$ , commercially at a high temperature. The magnesium oxide is reconverted to the chloride by hydrochloric acid.

Approximately two thirds of the chlorine manufactured is used in bleaching, chiefly of pulp and paper. Large quantities are also used in water purification as a germicide, and in the manufacture of organic dyes, explosives, and chemicals. It is usually liquefied and sold in cylinders, or converted into bleaching powder,  $\text{CaCl}(\text{ClO})$ , by action upon lime (Par. 5). The chlorine is again liberated from the bleaching powder upon the addition of acid. It was used extensively in the World War, at first directly as a poison gas, and later in the preparation of most of the other war gases, such as phosgene,  $\text{COCl}_2$ , and "mustard gas,"  $(\text{C}_2\text{H}_4\text{Cl})_2\text{S}$ .

**Bromine** may be prepared from the bromides by any of the methods used for chlorine. It is recovered commercially in Germany from the waste liquors of the potash industry,



and in America from various salt brines. The method depends upon the oxidation of bromide by chlorine. A commercial process has been developed for the recovery of bromine from sea water. Free bromine is liberated by chlorine, and precipitated as tribromoaniline upon the addition of aniline. The process is capable of extracting a pound of bromine from 1,800 gallons of sea water.

Liquid bromine is used in the preparation of most of the bromides and other compounds of the element. Like chlorine, it is used in the preparation of intermediate products in the synthesis of organic compounds, an example being the lead-tetraethyl now added in small amounts to gasoline to prevent "knocking." The major portion of the American production of bromine is consumed in this process; ethylene dibromide is the intermediate compound which is first formed.

**Iodine** is extracted from kelp by oxidation of the iodides with chlorine, or manganese dioxide in acid, or even by sulfuric acid. The principal source is, however, the Chile deposits containing sodium iodate and periodate. Iodine is liberated by reduction with sodium bisulfite:  $2\text{IO}_3^- + 5\text{HSO}_3^- = \text{I}_2 + 5\text{SO}_4^{--} + \text{H}_2\text{O} + 3\text{H}^+$ ; it is then removed and purified by sublimation.

Iodine is used in synthesis of aniline dyes, and iodides are employed somewhat in photography. It is also used in medicine as an antiseptic; in alcohol solution, known as tincture of iodine; in iodoform,  $\text{CHI}_3$ ; and as metallic iodides, in the prevention and cure of goiter, and other disorders of the thyroid gland.

**4. Physical Properties.**—Table I gives the colors of the elements in the gaseous state. In the liquid state, the colors are, of course, deeper. Liquid bromine and iodine are opaque except in very thin layers. Solid iodine is dark grey with a slight luster.

Solutions of chlorine and bromine in water show colors closely resembling those of the gases. Iodine dissolves in

many solvents, such as carbon tetrachloride, chloroform, and hexane, with a violet color resembling that of the vapor; but in solvents of high dielectric constant such as water and alcohol, its solution is brown. The progression in color in the gaseous halogens with increasing atomic weights is due to an absorption band, which in fluorine is nearly all in the ultraviolet, removing only a little of the visible light at the violet end of the spectrum, thus causing the transmitted light to have an excess of the complementary color, yellow. With chlorine this band has moved down into the blue, and so on, until with iodine the band removes the middle portions of the visible spectrum allowing only red and violet light to be transmitted.

The density in the gaseous state corresponds to molecules of 2 atoms each, which is confirmed by the figures for the same elements in solution. Heated to sufficiently high temperatures, the diatomic molecules gradually break down into single atoms. The dissociation of iodine in this way

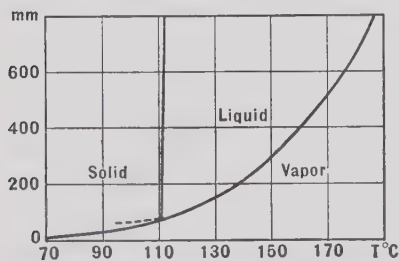


FIG. 1. Temperature-pressure diagram of iodine

becomes noticeable below 700°. Progressively higher temperatures would be necessary for the corresponding dissociation as we go from iodine to the lighter halogens, as indicated by the dissociation constants and heats of dissociation given in Table I.

Although solid iodine may be melted at 1 atmosphere pressure, it sublimes without melting below a pressure of 100 mm. as is indicated in the phase diagram, Fig. 1.

The halogens, with the exception of fluorine, are soluble in water (Table I). Chlorine and bromine form the hydrates,  $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$  and  $\text{Br}_2 \cdot 10\text{H}_2\text{O}$ . The former is stable up to 28.7° under a pressure of 6 atm. of chlorine, and the latter to 6.2° under a pressure of 93 mm. of bromine vapor.

Above  $28.7^{\circ}$ , chlorine under pressure forms with water two liquid layers. Bromine likewise forms two liquid layers, but the lower layer contains only a very small amount of water, 0.04 per cent at  $10^{\circ}$ .

**5. Reactions of the Halogens.**—The chemical behavior as related to atomic structure, has been discussed in Paragraph 1. Fluorine and chlorine are capable of oxidizing all metals, while bromine and iodine can oxidize all but the noblest. The products of these reactions are halides. The halogens do not react directly with oxygen or nitrogen. Fluorine reacts directly with all other elements except nitrogen, oxygen, chlorine, and the noble gases; and chlorine with all but these and carbon. Bromine and iodine are less reactive.

The reactions of the halogens with hydrogen are discussed in detail under the hydrogen halides. The halogens act upon many hydrocarbons, displacing hydrogen and forming the halogen acid: e.g.  $\text{CH}_4 + \text{Cl}_2 = \text{CH}_3\text{Cl} + \text{HCl}$ . They also unite directly with many unsaturated compounds:  $\text{C}_2\text{H}_4 + \text{Cl}_2 = \text{C}_2\text{H}_4\text{Cl}_2$  and  $\text{CO} + \text{Cl}_2 = \text{COCl}_2$ . They readily oxidize sulfur in most of its compounds: e.g.  $\text{CS}_2 + 2\text{Cl}_2 = \text{CCl}_4 + 2\text{S}$ . Excess of chlorine (or bromine but not iodine) will oxidize sulfur to sulfate in water solution.

TABLE II

OXIDATION-REDUCTION POTENTIALS OF HALOGEN-HALIDE COUPLES

	VOLTS <sub>25°</sub>
$\text{I}^- = \frac{1}{2}\text{I}_2 + e^-$ .....	— 0.535
$\text{Br}^- = \frac{1}{2}\text{Br}_2 + e^-$ .....	— 1.065
$\text{Cl}^- = \frac{1}{2}\text{Cl}_2 + e^-$ .....	— 1.358
$\text{F}^- = \frac{1}{2}\text{F}_2 + e^-$ .....	— 2.85

The oxidation-reduction potentials (Table II) of the free elements to the halide ions are extremely important, especially in connection with the general table (Append. II) in predicting many reactions. Thus, bromine will oxidize iodide,  $\text{I}^- + \frac{1}{2}\text{Br}_2 = \frac{1}{2}\text{I}_2 + \text{Br}^-$ , but will not oxidize chloride

or fluoride; and all of the halogens except iodine will oxidize ferrous ion to ferric:  $\text{Fe}^{++} = \text{Fe}^{+++} + e^{-}$ ,  $-0.77$  volt.

The halogens undergo two important **reactions with water**:



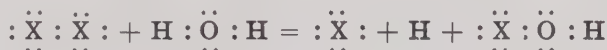
The potential values at  $25^{\circ}$  for reaction (1) in volts are:  $\text{F}_2$ , 2.0;  $\text{Cl}_2$ , 0.6;  $\text{Br}_2$ , 0.3, and  $\text{I}_2$ ,  $-0.3$  (i.e., in the reverse direction). Thus fluorine reacts vigorously with liquid water, liberating not only oxygen but ozone; chlorine reacts slowly in sunlight, liberating oxygen. On the other hand, moist hydrogen chloride gas reacts with oxygen with the aid of a catalyst to give a detectable amount of chlorine. Bromine liberates oxygen only very slowly from water, and the reaction is reversed if the hydrobromic acid has a high concentration. Iodine, on the other hand, is liberated from a solution of hydrogen iodide by oxygen, the speed of the reaction increasing rapidly with an increase in hydrogen ion concentration.

At a temperature of  $450^{\circ}$ , an equilibrium is reached between chlorine, steam, hydrogen chloride, and oxygen by means of which it is possible to convert two thirds of the hydrogen chloride into chlorine. This is the basis for the **Deacon process** once used for the manufacture of chlorine. Hydrogen bromide is completely oxidized to bromine at this temperature.

Reaction (2), the hydrolysis of the halogen, likewise takes place less completely, the higher the atomic weight of the halogen. In the case of fluorine the reaction cannot be observed because of the rapidity of reaction (1). With the other halogens a reversible equilibrium is established. At  $25^{\circ}$ , the equilibrium constants are: for  $\text{Cl}_2$ ,  $4.8 \times 10^{-4}$ ; for  $\text{Br}_2$ ,  $5 \times 10^{-9}$ ; for  $\text{I}_2$ ,  $3 \times 10^{-13}$ . The hydrolysis may in every case be largely repressed by the presence of acid, and increased by the addition of alkali. Thus, hydrogen chloride

added to hypochlorite liberates chlorine; and chlorine in sodium hydroxide solution is converted completely into chloride and hypochlorite. For a 0.01M Cl<sub>2</sub> solution, the above equilibrium constant corresponds to about 85 per cent hydrolysis. The electronic picture of the hydrolysis consists of a splitting of the halogen molecule and a union of the positive halogen atom with water.

Electron formulas



Ordinary formulas

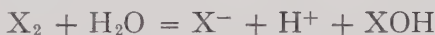


TABLE III

SUMMARY OF IMPORTANT REACTIONS OF HALOGENS

X = halogen

$X_2 + H_2 = 2HX$	cf. Par. 7
$X_2 + H_2O = 2HX + \frac{1}{2}O_2$	cf. Par. 5
$X_2 + H_2O = H^+ + X^- + HXO$	cf. Par. 5
$nX_2 + 2M = 2MX_n$	With most metals
$3X_2 + 2P = 2PX_3$	Also with As, Sb, Bi
$5X_2 + 2P = 2PX_5$	Not with I <sub>2</sub> . Also As, Sb with F <sub>2</sub> and Cl <sub>2</sub>
$X_2 + RH = RX + HX$	RH many organic hydrocarbons
$mX_2 + 2C_nH_m = XmHX + 2nC$	At high temperature. Less readily with Br <sub>2</sub> and I <sub>2</sub>
$X_2 + CO = COX_2$	With Cl <sub>2</sub> and Br <sub>2</sub>
$X_2 + SO_2 = SO_2X_2$	With F <sub>2</sub> and Cl <sub>2</sub>
$X_2 + H_2S = 2HX + S$	Excess H <sub>2</sub> S
$X_2 + 2S = S_2X_2$	With Cl <sub>2</sub> and Br <sub>2</sub> . F <sub>2</sub> forms SF <sub>6</sub> , Cl <sub>2</sub> also forms SCl <sub>4</sub>
$4X_2 + S_2O_3^{--} + 10OH^- = 2SO_4^{--} + 8X^- + 5H_2O$	
$I_2 + 2S_2O_3^{--} = S_4O_6^{--} + 2I^-$	Neutral or slightly acid solution
$3X_2 + 8NH_3 = 6NH_4X + N_2$	With F <sub>2</sub> , Cl <sub>2</sub> , Br <sub>2</sub>
$3Cl_2 + NH_4^+ = NCl_3 + 4H^+ + 3Cl^-$	I <sub>2</sub> forms NI <sub>3</sub> ·NH <sub>3</sub> with NH <sub>3</sub>
$2X_2 + TiO_2 + 2C = TiX_4 + 2CO$	With Cl <sub>2</sub> and Br <sub>2</sub> . Also SiO <sub>2</sub> , Cr <sub>2</sub> O <sub>3</sub> , etc.

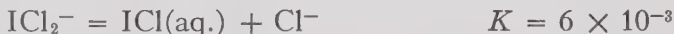
## COMPOUNDS OF THE HALOGENS

**6. Halogen Halides.**—In view of the great difference in the electronegative character of the halogens, it is not sur-

prising that the more positive form compounds with the more negative. Thus, iodine forms  $\text{IF}_7$  (m.p.  $5^\circ$ ),  $\text{IF}_5$  (m.p.  $-8^\circ$ ),  $\text{ICl}$  (2 forms m.p.  $\alpha$   $27.2^\circ$ ,  $\beta$   $13.9^\circ$ ),  $\text{ICl}_3$  (m.p.  $33^\circ$ ), and  $\text{IBr}$  (m.p.  $42^\circ$ ); and bromine forms  $\text{BrF}_5$  (m.p.  $-61.3$ ),  $\text{BrF}_3$  (m.p.  $9^\circ$ ),  $\text{BrF}$  (m.p.  $-33^\circ$ ) and  $\text{BrCl}$  (m.p.  $-66^\circ$ ) and chlorine forms  $\text{ClF}_3$  (m.p.  $-83^\circ$ ) and  $\text{ClF}$  (m.p.  $-156^\circ$ ). The positive character of the larger halogen in these compounds is indicated, for example, by electrolysis of liquid iodine chloride,  $\text{ICl}$ , and also by its solution in sulfur dioxide, whereby iodine is liberated at the cathode, and chlorine at the anode. Hydrolysis gives the corresponding oxy-acid of the positive halogen, and the halide ion of the other.  $\text{IF}_5 + 3\text{H}_2\text{O} = \text{IO}_3^- + 5\text{F}^- + 6\text{H}^+$ . Because of the instability of the lower oxy-acids, the first step is not always realized: thus,  $5\text{ICl} + 3\text{H}_2\text{O} = 2\text{I}_2 + 5\text{Cl}^- + \text{IO}_3^- + 6\text{H}^+$ .

**Iodine monochloride** is formed by the direct action of chlorine upon iodine, and by the reaction,  $\text{HIO} + \text{HCl} = \text{ICl} + \text{H}_2\text{O}$ . By the latter reaction, iodine monochloride is often formed through the reduction of iodates, or the oxidation of iodides in moderately concentrated hydrochloric acid. It hydrolyzes in dilute acid.

The chloride reacts with excess chloride ion to form the complex ion



and the potential of the oxidation of iodine to the complex ion,



is given as  $-1.06$  volts. (Cf. Par. 18.) If the formation of iodine monochloride in concentrated hydrochloric acid is accompanied by the liberation of chlorine, iodine trichloride,  $\text{ICl}_3$ , results. Salts, such as  $\text{KICl}_4$ , are known.

**7. Hydrogen Halides. Preparation.**—The hydrogen halides may be formed by direct union of the elements. As



shown in Table IV, the reaction:  $X_2 + H_2 = 2HX$ , decreases in energy with increasing atomic weight of the halogen. Fluorine and hydrogen combine instantly, even at a temperature of  $-253^\circ \text{C.}$ , where fluorine is solid and hydrogen liquid. The rate of combination of hydrogen and chlorine is slow in the dark, but takes place with explosive violence in the sunlight, or at  $250^\circ \text{C.}$  The increased speed under these conditions is doubtless due to the absorption of radiant energy by the chlorine molecule, and the more rapid reaction of this activated molecule. Of course, as soon as a few molecules react, enough energy is liberated to activate many molecules. Some idea of the force holding the  $\text{HCl}$  molecules together is given by the consideration that the formation from hydrogen and chlorine involves the dissociation of  $\text{Cl}_2$ , 56,900 cal., and  $\text{H}_2$ , 103,730. The reactions of hydrogen with bromine and iodine are very slow at room temperature, and are catalyzed by light and by platinum at higher temperature.

TABLE IV  
PROPERTY OF HYDROGEN HALIDES

	HF	HCl	HBr	HI
Boiling point.....	20	— 85	— 67	— 36
Melting point.....	— 83	— 114	— 87	— 51
$\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{X}_2 = \text{HX}$	Heat kcal....	22.0	13.5	— 0.8
	Per cent dissociation at $1000^\circ$ ...			
$\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{X}_2 = \text{HX}$		$1.34 \times 10^{-13}$	0.144	29.0
Solubility in water 1 at. and $20^\circ \text{C.}$ g. per 100 g. of solution.....	35.3	42	49	57
Heat of solution at infinite dilution, kcal.....	11.6	17.3	19.9	19.2
Constant boiling mixture, 1 at.	Temp.....	120	110	126
	Density.....	1.14	1.10	1.49
	Wt. per cent of acid....	35.37	20.24	47
Dielectric constant of liquid.....	66	9	6	3
Heat of neutralization of dilute acid in kcal.....	16.2	13.4	13.4	13.4

Hydrogen fluoride and chloride are usually prepared by the action of the less volatile sulfuric acid upon a halide salt,

such as  $\text{CaF}_2$  and  $\text{NaCl}$ . In the case of hydrogen chloride, the reaction is the first step in the LeBlanc carbonate process (cf. IV—13). The acid sulfate is first formed:  $\text{NaCl} + \text{H}_2\text{SO}_4 = \text{HCl} + \text{NaHSO}_4$ , and the mixture is heated to a temperature of about  $500^\circ$ , in order to complete the second step:  $\text{NaCl} + \text{NaHSO}_4 = \text{HCl} + \text{Na}_2\text{SO}_4$ . Because of the oxidation of bromide and iodide by hot concentrated sulfuric acid,  $\text{H}_2\text{SO}_4 + 2\text{HI} = \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$ , this acid is replaced usually by phosphoric acid in the preparation of hydrogen bromide and iodide. The acids may be prepared by the hydrolysis of the halides of the more negative elements, such as phosphorus, sulfur, or arsenic:  $\text{PBr}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{HBr}$ . The halides of the noble metals may be reduced with hydrogen at a high temperature to form the hydrogen halide:  $2\text{AgCl} + \text{H}_2 = 2\text{Ag} + 2\text{HCl}$ . These acids are also formed by the action of the halogens upon many organic hydrocarbons:  $\text{C}_6\text{H}_6 + \text{Br}_2 = \text{C}_6\text{H}_5\text{Br} + \text{HBr}$ . A solution of hydrogen iodide is conveniently prepared by the action of hydrogen sulfide upon a suspension of iodine in water:  $\text{H}_2\text{S} + \text{I}_2 = \text{S} + 2\text{HI}(\text{aq.})$ . With gaseous  $\text{HI}$  this reaction is reversible.

**8. Properties.**—The hydrogen halides are all colorless gases; they possess a disagreeable pungent odor, fume strongly in moist air, are extremely soluble in water; their water solutions, with the exception of hydrogen fluoride, are strongly acidic. The water solutions are called hydrofluoric acid, hydrochloric acid, etc. In the pure liquid state, they have a low electrical conductivity, of about the same magnitude as that of pure water. The approximate values for the dielectric constants of the liquids indicate that the electrical polarization decreases with increasing molecular weight. Hydrogen fluoride gas polymerizes, forming  $(\text{HF})_6$ . At  $20^\circ \text{C.}$  and 745 mm., 80 per cent of the  $\text{HF}$  is so polymerized. This property is not shown by the other gases.

The water solutions exhibit the phenomena of **boiling point maxima**. The temperature composition diagram for

hydrochloric acid is given in Fig. 2. The curve represents the temperature at which a given composition of the acid will boil, i.e. the temperature at which the sum of the pressures of hydrogen chloride and water equals atmospheric pressure. As a given solution boils, its composition changes toward that of the maximum boiling mixture. When this composition is reached, the solution boils without further change in composition. The composition of the maximum boiling mixture depends upon the total pressure. For hydrogen chloride, 1 atmosphere, the value is 20.24 per cent HCl and the temperature  $110^{\circ}$ ; for 2,500 mm., the composition is 18 per cent; and for 50 mm. it is 23.2 per cent. Advantage is often taken of these fixed concentrations to prepare acids of known concentrations for quantitative analysis.

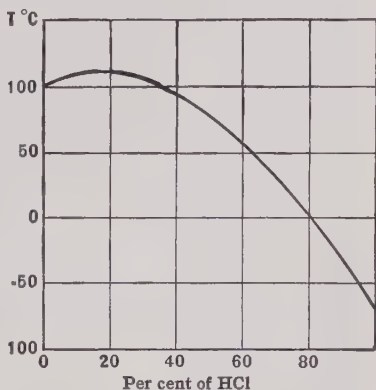


FIG. 2. Boiling point-composition curve for HCl.

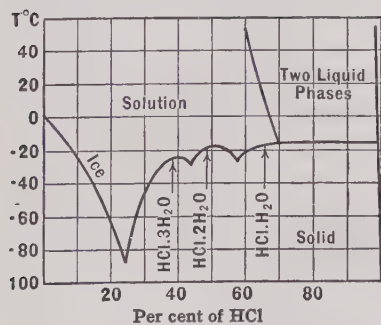


FIG. 3. The system water-hydrogen chloride.

tetrahydrate; and hydrogen iodide, tri-, and tetrahydrates.

The **ionization** of these acids in dilute solution is 100 per cent, as judged by the lowering of vapor pressure and freezing points, and by electrical conductivity. The apparent ionization at higher concentrations is discussed in Ap-

pendix IV. Hydrofluoric acid is much weaker than the other acids ( $\text{HF}_{\text{aq}} = \text{H}^+ + \text{F}^-$ ,  $K = 7.2 \times 10^{-4}$ ). In fairly concentrated solutions, it forms the ion  $\text{HF}_2^-$  ( $\text{F}^- + \text{HF} = \text{HF}_2^-$ ,  $K = 5.5$ ). In dilute solutions, its heat of neutralization is about 3 kcal. more than that of typically strong acids, which is unusual, as the heat of neutralization of

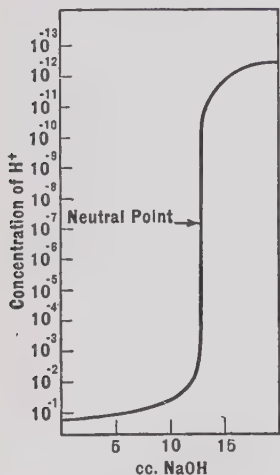


FIG. 4. Titration of HCl with NaOH.

other weak acids is less than that of strong acids. The change of concentration of hydrogen ion in hydrochloric acid, upon titration with hydroxide, is given in Fig. 4.

**9. Uses.**—Hydrogen fluoride is used in etching glass. This remarkable property results from the action of hydrogen fluoride upon silicon dioxide:  $\text{SiO}_2 + 4\text{HF} = \text{SiF}_4 + 2\text{H}_2\text{O}$ . The silicon fluoride escapes as a gas. Etched designs, such as buret graduations, are made by covering the glass with paraffin, which is scraped away where etching is desired, and then treating with a solution of the

acid. A mixture of ammonium fluoride and hydrogen fluoride is used in frosting glass. The acid is also used in quantitative analysis, in dissolving complex silicates, since most silicates are decomposed through the removal of the silica. It has certain application in the curing of crude rubber, in cleaning the exterior of stone buildings, and in cleaning castings.

Hydrochloric acid is used in the preparation of metal chlorides, especially those of zinc and tin; in cleaning metal surfaces, particularly iron before galvanizing; and in the manufacture of glue, soap, glucose, dyes, and many other materials.

**10. Halides and Halide Ions.—Fluoride.** The fluorides of lithium, the alkaline earth, and the rare earth metals are

sparingly soluble. Fluoride forms more stable complexes than do the other halides with small positive ions, for example,  $\text{BF}_4^-$ ,  $\text{SiF}_6^{--}$ ,  $\text{AlF}_6^{---}$ . These complexes are analogous to the corresponding oxygen acids, and their stability is doubtless due to high electrostatic attraction for the small fluoride ions. On the other hand, the fluoride ion is not as polarizable as the larger halides (cf. VII—2), and does not readily form coordination complexes with the ions of the noble metals.

The metal fluorides form acid salts of the type  $\text{KHF}_2$ , and even  $\text{KH}_3\text{F}_4$ , and the crystal structure of these compounds indicates that the hydrogen ion serves to bind two fluoride ions together:



**11. Chloride.** Among the most important sparingly soluble chlorides are those of  $\text{Ag}^+$ ,  $\text{Hg}_2^{++}$ ,  $\text{Tl}^+$ ,  $\text{Cu}^+$ ,  $\text{Pb}^{++}$ ,  $\text{Au}^+$ ,  $\text{Pt}^{++}$ ,  $\text{Pt}^{++++}$ ,  $\text{SbO}^+$ , and  $\text{BiO}^+$ .

The solubility of all metallic chlorides is decreased by a small excess of chloride ion, but a larger concentration often leads to an increase in solubility through the formation of complex ions. The alkali and alkaline earth elements do not form complex chlorides, but practically all of the subgroup and transition elements do. Thus ions of the type  $[\text{XCl}_6]^{-6+n}$  are formed by the + 3 ions of the following elements: Al, In, Ir, Mo, As, Rh, Sc, Tl, and V; the + 4 ions of: Ge, Hf, Ir, Os, Pd, Pt, Pb, Re, Sb, Si, Sn, Ti, Tl, and Zr; and the + 5 ions of Cb, Sb, and Ta. Ions of the type  $[\text{XCl}_4]^{-4+n}$  are formed by the + 2 ions of Be, Co, Cu, Cd, Hg, Pd, Pt, and Zn, and by the + 3 ions of Au, B, Bi, In, Re, Tl, V, and Y. With  $\text{Ag}^+$  and  $\text{Cu}^+$  the complex chlorides are  $\text{XCl}_2^-$ ,  $\text{XCl}_3^{--}$  and possibly  $\text{XCl}_4^{---}$ . The ions  $[\text{XCl}_4]^{-6+n}$  are octahedral but the  $[\text{XCl}_4]^{-4+n}$  are of the two types, tetrahedral and square planar.

There is some evidence for the formation of trichloride

$\text{Cl}_3^-$  when chlorine is passed into concentrated hydrogen chloride (see Triiodide below).

Certain of the chlorides, especially the volatile chlorides of metals of higher valence, may be prepared by the action of chlorine upon a heated mixture of the oxide and carbon: e.g.  $\text{TiO}_2 + 2\text{Cl}_2 + 2\text{C} = \text{TiCl}_4 + 2\text{CO}$ .

Chlorides of the non-metals, e.g.  $\text{CCl}_4$ ,  $\text{PCl}_5$ ,  $\text{SCl}_4$ , are discussed under these elements.

**Bromide.** Bromide ion is very similar to chloride ion in the character of its slightly soluble compounds and complex ions, though in general the sparingly soluble bromides are somewhat less soluble than the corresponding chlorides.

Alkali bromides are usually prepared from bromine, by first forming ferrous bromide by action of bromine upon iron, and then carrying out the double decomposition with the alkali carbonate: e.g.  $\text{FeBr}_2 + \text{K}_2\text{CO}_3 = \text{FeCO}_3 + 2\text{KBr}$ .

**Iodide.** The iodide ion, being the largest and most easily polarized (cf. VII—2) of the halides, forms very insoluble salts, and very stable coordination complex ions with the subgroup metals. The stability of many of these compounds is limited, however, by the ease of oxidation of iodide to the free element. The method of formation of the alkali iodides is similar to that of the bromides, *vide supra*.

Iodide ion readily dissolves iodine with the formation of **triiodide**:  $\text{I}^- + \text{I}_2 (\text{aq.}) = \text{I}_3^-$ , the constant  $(\text{I}^-)(\text{I}_2)/(\text{I}_3^-) = 1.4 \times 10^{-3}$  at  $25^\circ$ . This reaction is important as a means of bringing iodine into aqueous solution. Higher polyiodides are formed in very concentrated solutions.

In neutral solution, iodide is not readily oxidized by oxygen in the air; but in acid solution, the reaction becomes rapid:  $6\text{I}^- + \text{O}_2 + 4\text{H}^+ = 2\text{I}_3^- + 2\text{H}_2\text{O}$ . The quantitative oxidation of iodide by powerful oxidizing agents, e.g.  $\text{H}_2\text{O}_2$  or  $\text{KMnO}_4$ , is extremely important in quantitative analysis (Par. 21).



**12. Oxygen Compounds of the Halogens.**—Fluorine forms the fairly stable oxide,  $F_2O$ , and at low temperatures the oxides  $F_2O_2$  and  $F_2O_3$ . Bromine forms no stable oxides, though the unstable oxides  $Br_2O$  and  $BrO_2$  have recently been prepared. Chlorine forms the oxides  $Cl_2O$ ,  $ClO_2$ , and  $Cl_2O_7$ ; and iodine, the oxides  $I_2O_4$  and  $I_2O_5$ . A number of additional oxides as  $ClO_3$ ,  $ClO_4$ , and  $I_2O_3$  have been described, but they are extremely unstable. None of these oxides are formed by direct union of the elements. The oxides with an odd oxidation state of the halogen are anhydrides of the corresponding acids. The oxygen acids of the halogens are given in the following summary. The halous acids and their salts are of the least importance. Indeed the existence of  $HBrO_2$  and  $HIO_2$  is but momentary, usually as an intermediate reaction step.

TABLE V  
OXYGEN ACIDS OF THE HALOGENS

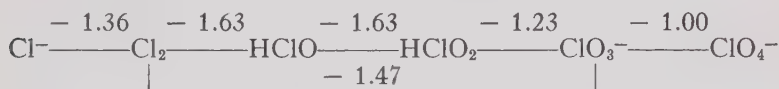
OXIDATION STATE	NAME	CHLORINE	BROMINE	IODINE	NAME OF ION
+1	hypo-ous	HClO	HBrO	HIO	hypo-ite
+3	-ous	HClO <sub>2</sub>	(HBrO <sub>2</sub> )	(HIO <sub>2</sub> )	-ite
+5	-ic	HClO <sub>3</sub>	HBrO <sub>3</sub>	HIO <sub>3</sub>	-ate
+7	per-ic	HClO <sub>4</sub>	—	HIO <sub>4</sub> and $H_5IO_6$	per-ate

TABLE VI  
OXIDATION-REDUCTION POTENTIALS OF HALOGEN ACIDS AND IONS  
Volts<sub>25°</sub>

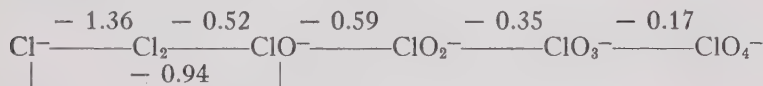
COUPLE	Cl	Br	I
<i>Acidic solution</i>			
$\frac{1}{2}X_2 + 4H_2O = 8H^+ + XO_4^- + 7e^-$	- 1.34	—	(- 1.38)
$\frac{1}{2}X_2 + 3H_2O = 6H^+ + XO_3^- + 5e^-$	- 1.47	- 1.52	- 1.195
$\frac{1}{2}X_2 + 2H_2O = 3H^+ + HXO_2 + 3e^-$	- 1.63	—	—
$\frac{1}{2}X_2 + H_2O = H^+ + HXO + e^-$	- 1.63	- 1.59	- 1.45
<i>Basic solution</i>			
$X^- + 8OH^- = XO_4^- + 4H_2O + 8e^-$	- 0.51	- 0.61	(- 0.38)
$X^- + 6OH^- = XO_3^- + 3H_2O + 6e^-$	- 0.62	—	- 0.26
$X^- + 4OH^- = XO_2^- + 2H_2O + 4e^-$	- 0.76	—	—
$X^- + 2OH^- = XO^- + H_2O + 2e^-$	- 0.94	- 0.76	- 0.49

The halogen oxyacids are powerful oxidizing agents, as is indicated in the table on page 169, which gives the potential in volts for their reductions to the elements in acid and to the halides in alkaline solutions. These values may be used to calculate the potentials of the reduction in steps. The potentials for the case of chlorine are given in the following scheme:

*Acidic solution:*



*Basic solution:*



Since the oxyacids of chlorine and bromine are sufficiently powerful oxidizing agents to liberate oxygen from water ( $2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4e^-$ ,  $-1.23$  volts), it follows that water solutions of these acids are unstable. These decompositions are slow, but are catalyzed by certain substances.

It may also be observed from the table that the oxidizing potentials of the halates decrease with increasing atomic weight, so that iodine will replace bromine in bromate, and bromine will replace chlorine in chlorate: e.g.  $2\text{BrO}_3^- + \text{I}_2 = 2\text{IO}_3^- + \text{Br}_2$ . The reactions take place in highly acid solution, and while they are often called replacement reactions, they are in reality complicated oxidation-reduction reactions.

With the exception of perchloric acid, the potentials are greater than those of the halogens to halide (cf. Table II); hence, these acids are reduced by the halide ion.  $\text{HClO} + \text{H}^+ + \text{Cl}^- = \text{Cl}_2 + \text{H}_2\text{O}$ ;  $\text{IO}_3^- + 6\text{H}^+ + 5\text{I}^- = 3\text{I}_2 + 3\text{H}_2\text{O}$ .

The  $+1$  state is unstable in regard to its own oxidation

and reduction into halate and halide; thus  $3\text{XO}^- = \text{XO}_3^- + 2\text{X}^-$ . Because of the reduction of the oxygen acids by the halide as mentioned above, this reaction in acid approaches the stoichiometric equation:  $5\text{HXO} = \text{XO}_3^- + \text{H}^+ + 2\text{X}_2 + 2\text{H}_2\text{O}$ . The speed of decomposition increases rapidly in order from hypochlorous to hypoiodous. In the case of chlorate ion, we encounter instability with respect to perchlorate and chloride ions, according to the equation:  $4\text{ClO}_3^- = 3\text{ClO}_4^- + \text{Cl}^-$ . This occurs readily in the fused state.

**13. Oxides of Fluorine.**—The oxide (probably better called the fluoride),  $\text{F}_2\text{O}$ , is formed by passing fluorine into a dilute solution of sodium hydroxide.



The oxide boils at  $-146.5^\circ$  and in the absence of reducing agents is a stable gas at room temperature. It does not react with water but is a very powerful oxidizing agent (potential  $\text{F}^-$ - $\text{F}_2\text{O}$  couple in acid  $-2.1$ ). The oxide  $\text{F}_2\text{O}_2$  is formed at low temperatures by the action of an electrical discharge on a mixture of the two gases. It is unstable above  $-100^\circ \text{C}$ .

**14. Chlorine Monoxide and Hypochlorite.**—Chlorine monoxide,  $\text{Cl}_2\text{O}$ , is the anhydride of hypochlorous acid,  $\text{HClO}$ . Its reaction with water,  $\text{Cl}_2\text{O} + \text{H}_2\text{O} = 2\text{HClO}$ , is reversible. The gas, at 1 atmosphere and  $0^\circ$ , is in equilibrium with a solution containing about 200 volumes of the gas per volume of solution. It is most conveniently prepared by the action of chlorine upon finely divided mercuric oxide:  $2\text{HgO} + 2\text{Cl}_2 = \text{Cl}_2\text{O} + \text{Hg}_2\text{OCl}_2$ . The reaction is carried out at about  $0^\circ$ , at which temperature the gas condenses to a liquid. The gas and liquid have a deep yellowish red color, and are highly explosive.

The hydrolysis of chlorine (Par. 6) yields hydrochloric acid and hypochlorous acid. The equilibrium is displaced by hydroxide through the neutralization of these acids:

$\text{Cl}_2 + 2\text{OH}^- = \text{H}_2\text{O} + \text{Cl}^- + \text{ClO}^-$ . A solution containing chloride and hypochlorite is easily prepared by the electrolysis of a solution of  $\text{NaCl}$  in a cell permitting the chlorine produced at the anode to react with the  $\text{OH}^-$  produced at the cathode. This solution is a cheap, efficient, and widely used disinfectant and bleaching agent. For household use, it can be purchased under the name of "chlorox."

When chlorine is passed over slaked lime, a reaction occurs which is closely related to the one given above:  $\text{Cl}_2 + \text{Ca}(\text{OH})_2 = \text{H}_2\text{O} + \text{CaCl}(\text{ClO})$ . The two ions,  $\text{Cl}^-$  and  $\text{ClO}^-$ , here remain attached to the same calcium ion. The resulting compound is known as "**bleaching powder**," or "**chloride of lime**." Upon solution in water it gives the corresponding ions; hence, when an excess of acid is added, chlorine is liberated, corresponding to the shift of the hydrolysis equilibrium of chlorine. Bleaching powder is extensively used for bleaching and disinfecting. Any solution containing both  $\text{Cl}^-$  and  $\text{ClO}^-$  can be made to yield chlorine in almost any desired concentration by suitably fixing the hydrogen ion concentration. However small the equilibrium concentration of chlorine, it will nevertheless be approximately maintained as the chlorine is used up. Such a solution is much used in surgery under the name "Dakin's solution."

One equivalent of acid, acting upon bleaching powder, liberates the weak hypochlorous acid,  $\text{HClO}$ , which may be distilled from the solution and thus separated from chloride ion. The dissociation constant of the acid is  $5.6 \times 10^{-8}$ .

The familiar odor of bleaching powder is due to hypochlorous acid liberated by the carbonic acid of the air.

Hypochlorite solutions readily give off oxygen (Par. 5) in the presence of a catalyst, e.g. cobalt hydroxide. Heated in the absence of a catalyst, the following reaction occurs:  $3\text{ClO}^- = \text{ClO}_3^- + 2\text{Cl}^-$ . The rate is increased if the solution is slightly acid.

**15. Chlorites and Chlorine Dioxide.**—Although chlorine dioxide and the chlorites are of different oxidation states, they are discussed together because of the formation of chlorite by the reaction of the oxide in alkaline solution:  $2\text{OH}^- + 2\text{ClO}_2 = \text{ClO}_2^- + \text{ClO}_3^- + \text{H}_2\text{O}$ . Chlorine dioxide is one of the few “odd molecules” : $\ddot{\text{O}}:\ddot{\text{Cl}}:\ddot{\text{O}}:$ , i.e. possessing an odd number of electrons; and the mechanism of the above reaction may be considered to be the transfer of the odd electron from one molecule of the oxide to another, forming  $\text{ClO}_2^-$  and  $\text{ClO}_2^+$ . The latter adds a molecule of hydroxide to form  $\text{HClO}_3$ . Chlorous acid is unstable except in very dilute solutions, and its salts are also unstable, decomposing to give (a) oxygen and chloride, and (b) chlorate and chloride.

The formation of chlorine dioxide from chloric acid is mentioned below (Par. 16). It may also be prepared by the action of chloric acid upon oxalic acid:  $2\text{HClO}_3 + \text{H}_2\text{C}_2\text{O}_4 = 2\text{ClO}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O}$ . Chlorine dioxide is a gas at ordinary temperatures, and, like most substances having “odd molecules,” is colored, in this case a dark yellow, and moreover is extremely unstable.

Approximate values for the potentials of the dioxide are:

	VOLTS <sub>25°</sub>
$2\text{H}_2\text{O} + \text{Cl}^- = \text{ClO}_2 + 4\text{H}^+ + 5e^-$ .....	- 1.50
$4\text{OH}^- + \text{Cl}^- = \text{ClO}_2 + 2\text{H}_2\text{O} + 5e^-$ .....	- 0.8

**16. Chloric Acid and Chlorates.**—Chlorates are easily prepared by decomposition of the hypochlorite (Par. 12). The process may be carried out, either by passing chlorine into hot alkaline solution, or by the electrolysis of a hot chloride solution with agitation so as to bring the chlorine from the anode into contact with the hydroxide of the cathode. Chloric acid decomposes upon distillation, and cannot be prepared in the pure state. A solution may be obtained by treating a solution of barium chlorate with dilute sulfuric acid:  $\text{Ba}^{++} + 2\text{ClO}_3^- + 2\text{H}^+ + \text{SO}_4^{--} = \text{BaSO}_4 + 2\text{H}^+$

+  $2\text{ClO}_3^-$ . It is a strong acid and is much less stable than its salts. In addition to the decomposition into perchlorate and chloride and into oxygen and chloride, it may decompose according to the equation:  $4\text{HClO}_3 = 4\text{ClO}_2 + \text{O}_2 + 2\text{H}_2\text{O}$ . If concentrated sulfuric acid is added to solid chlorate, the above reaction takes place, and usually the  $\text{ClO}_2$  formed explodes with great violence.

**Potassium chlorate** is the most important salt of chloric acid. While readily soluble in hot water, its solubility is but 3.1 g. per 100 grams of water at  $0^\circ$ . Advantage is taken of this behavior in preparing potassium chlorate by adding potassium chloride to a hot solution containing chlorate ion made from calcium hydroxide and chlorine, and then cooling.

Potassium chlorate decomposes at moderate temperatures as follows:  $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$ . This reaction is catalyzed by manganese dioxide, and furnishes a convenient laboratory method for the preparation of oxygen. If carefully heated to avoid the evolution of oxygen, potassium chlorate may be converted into the perchlorate:  $4\text{KClO}_3 = 3\text{KClO}_4 + \text{KCl}$ .

The oxidizing power of potassium chlorate renders it useful in making matches and pyrotechnics. Explosive mixtures may be made, using potassium chlorate with combustible substances such as charcoal, sugar, or sulfur; they are too treacherous to be of practical value. A solution of potassium chlorate is sometimes used as a gargle in throat infections.

All of the chlorates are at least moderately soluble. **Lithium chlorate** is one of the most soluble of all salts, 100 g. of water dissolves 315 g. of the salt at  $18^\circ$ .

**17. Perchloric Acid and Perchlorates.**—As mentioned in the previous section, perchlorates may be prepared by carefully heating chlorates. They may also be prepared by anodic oxidation in the electrolysis of concentrated chlorate solutions:  $\text{ClO}_3^- + \text{H}_2\text{O} = \text{ClO}_4^- + 2\text{H}^+ + 2e^-$ . Although



this half reaction only requires a calculated potential of about one volt, it is difficult to find an oxidizing agent capable of bringing it about, since the oxidizing agent must at the same time be more powerful than chlorate; peroxysulfuric acid or sodium bismuthate may, however, be used for this purpose. Perchloric acid may be distilled from a solution formed by the addition of sulfuric acid to a perchlorate. This reaction is subject to violent explosions. The anhydrous acid is best prepared by the action of nitric and hydrochloric acids upon a solution of ammonium perchlorate. The pure acid is a volatile liquid at ordinary temperatures, and decomposes at  $92^{\circ}$  under atmospheric pressure. The acid reacts explosively with strong reducing agents. It combines with water to form the solid hydrate,  $\text{HClO}_4 \cdot \text{H}_2\text{O}$ , with the evolution of much heat. It is interesting to note that this hydrate,  $\text{OH}_3\text{ClO}_4$ , has the same crystal structure as  $\text{NH}_4\text{ClO}_4$ . The addition of phosphorus pentoxide to perchloric acid, cooled below  $0^{\circ}$ , results in formation of **perchloric anhydride**:  $6\text{HClO}_4 + \text{P}_2\text{O}_5 = 2\text{H}_3\text{PO}_4 + 3\text{Cl}_2\text{O}_7$ . This oxide is a colorless liquid which may be heated to its boiling point,  $82^{\circ}$ , without decomposition. It is easily detonated, however, by a sudden shock.

The perchlorates are safer to handle than the chlorates. They are used in matches, fireworks, and explosives. They are as a rule readily soluble, potassium, rubidium, and cesium perchlorates being the least soluble. Due to its slight solubility, potassium perchlorate is easily prepared and purified. It is probably the most important of the salts.

If silver perchlorate is treated with bromine, silver bromide and **free perchlorate radical**,  $\text{ClO}_4$ , result:  $2\text{AgClO}_4 + \text{Br}_2 = 2\text{AgBr} + 2\text{ClO}_4$ . This substance also has an odd number of valence electrons, and is extremely reactive and unstable.

**18. Hypobromite and Hypiodite.**—The hydrolysis of the halogens decreases markedly with increasing atomic weight (Par. 5); however, in strongly alkaline solution both bro-

mine and iodine are almost completely converted into the halide and hypohalite. Hypobromous acid, and more especially hypoiodous acid are very unstable, decomposing almost immediately into the halide and halate. They are also extremely weak acids. In fact, the reaction,  $\text{IOH} + \text{HCl} = \text{ICl} + \text{H}_2\text{O}$ , indicates certain basic tendencies in the latter. Hypobromites and hypoiodites decompose much more readily than hypochlorites to give halate and halide. The unstable **monoxide**,  $\text{Br}_2\text{O}$ , has been prepared by the action of bromine upon mercuric oxide at  $50^\circ$ :  $2\text{HgO} + 2\text{Br}_2 = \text{Br}_2\text{O} + \text{Hg}_2\text{OBr}_2$ .

**19. Bromate and Iodate.**—In addition to the methods of preparation analogous to the chlorine compounds, bromic and iodic acids may be prepared from the elements by the action of powerful oxidizing agents such as hypochlorous, chloric, and nitric acids, and hydrogen peroxide. Bromic acid cannot be prepared in the pure state, as the concentrated solutions decompose, forming oxygen and bromine. The bromates are in general less soluble than the chlorates, and may be distinguished from the latter by the insolubility of silver bromate. They have some industrial applications as oxidizing agents.

Iodic acid is a white solid and is very soluble in water. It is most conveniently prepared in a pure state by the action of a slight excess of chloric acid upon iodine, or by the action of hydrogen peroxide in acid solution upon iodine. It may be dehydrated by careful heating to form the **pentoxide**,  $\text{I}_2\text{O}_5$ . This is a white solid which may be heated to about  $300^\circ$  before decomposition becomes rapid. Sodium iodate, occurring in the Chile nitre beds, has been mentioned as the most important source of the element. The iodates are much less soluble and much more stable than the other halates, and are easily distinguished from them by the insolubility of their barium and lead salts. Iodates in highly acid solution oxidize chloride. Neither the acid nor the salts show any tendency to decompose to form the perio-

dates. Potassium iodate and bi-iodate,  $\text{KH}(\text{IO}_3)_2$ , are of considerable importance in analytical chemistry (Par. 21), because of the quantitative reduction to iodine in dilute acid and to iodine chloride in moderately concentrated hydrochloric acid by many reducing agents. The potential for the latter reduction is  $-1.23$  volts corresponding to the half reaction:



**19. Iodine Tetroxide.**—The oxide,  $\text{I}_2\text{O}_4$ , may be prepared by the action of concentrated sulfuric acid upon iodic acid, similar to the preparation of chlorine dioxide. It reacts with water according to the equation:  $5\text{I}_2\text{O}_4 + 4\text{H}_2\text{O} = 8\text{HIO}_3 + \text{I}_2$ . With sulfuric acid, it forms a complex compound,  $(\text{I}_2\text{O}_4)\text{H}_2\text{SO}_4$ .

**20. Periodic Acid and Periodates.**—Strong oxidizing agents convert the iodates into periodates. There is a long series of polybasic periodic acids which may be considered as derived from the anhydride,  $\text{I}_2\text{O}_7$ , by the addition of  $n$  molecules of water,  $\text{I}_2\text{O}_7 \cdot n\text{H}_2\text{O}$ , where  $n$  has the values 1 to 7: e.g.  $\text{I}_2\text{O}_7 + \text{H}_2\text{O} = 2\text{HIO}_4$ ;  $\text{I}_2\text{O}_7 + 2\text{H}_2\text{O} = \text{H}_4\text{I}_2\text{O}_9$ ;  $\text{I}_2\text{O}_7 + 7\text{H}_2\text{O} = 2\text{H}_7\text{IO}_7$ . The existence of  $\text{H}_7\text{IO}_7$ , or its salts, is somewhat doubtful, but the acid,  $\text{H}_5\text{IO}_6$ , is probably the principal constituent of the water solution. The constant for the first ionization is  $2.3 \times 10^{-2}$  and for the second about  $10^{-6}$ . The second step of the neutralization appears also to involve the equilibrium,  $2\text{H}_3\text{IO}_6^{--} = \text{I}_2\text{O}_9^{-4} + 3\text{H}_2\text{O}$ . The higher polybasic acids may be dehydrated to form the meta acid,  $\text{HIO}_4$ ; but the anhydride,  $\text{I}_2\text{O}_7$ , cannot be prepared, as further heating causes decomposition into oxygen and the pentoxide. The fact that the iodine atom in periodic acid is surrounded by as many as six oxygen atoms, while the chlorine atom in perchloric acid is limited to four may be correlated with the larger size of the iodine atom.

The preparation of periodates is usually accomplished by heating iodate with chlorine in alkaline solution:  $2\text{Na}^+$

+  $\text{IO}_3^- + 3\text{OH}^- + \text{Cl}_2 = \text{Na}_2\text{H}_3\text{IO}_6 + 2\text{Cl}^-$ . The product, disodium paraperiodate, is but moderately soluble. In highly acid solution the periodates are extremely powerful oxidizing agents, being capable of oxidizing manganous ion to permanganate, which requires a potential of  $-1.5$  volts. Excess periodate, in even low acid concentration, is reduced to iodate by iodide:  $2\text{H}^+ + \text{IO}_4^- + 2\text{I}^- = \text{IO}_3^- + \text{I}_2 + \text{H}_2\text{O}$ . With excess iodide, the product is triiodide.

**21. Analytical Properties.**—Advantage is taken of the insolubility of silver chloride, bromide, and iodide in both the qualitative and quantitative determination of these halides (cf. VII—27). Iodides and bromides are readily distinguished from chlorides by the liberation of bromine or iodine by chlorine water, and the production of the characteristic colors upon extraction of the free halogen with carbon disulfide.

The oxygen compounds of the halogens may be determined qualitatively by the reduction to the free element or halide, and identified as such. Quantitatively they may be reduced by excess reducing agent, such as stannous chloride, or titanous chloride, and the excess reducing agent titrated with permanganate; or they may be reduced with excess iodide and the iodine formed titrated (at low  $\text{H}^+$ ) with thiosulfate:  $\text{I}_3^- + 2\text{S}_2\text{O}_3^{--} = 3\text{I}^- + \text{S}_4\text{O}_6^{--}$ .

The reaction just given for the oxidation of thiosulfate by iodine or triiodide is one of the most important in chemical analysis. It provides a general method for the determination of oxidizing agents, as indicated above, by the addition of excess iodide and the titration of the iodine by thiosulfate. As an end point indicator in this titration, soluble starch is added to the solution, giving a deep blue color as long as an appreciable concentration of iodine is present. Strong reducing agents may be titrated by direct oxidation with triiodide.

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# Chapter XI

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## GROUP V. N, P, As, Sb, Bi

1. The elements of Group V, nitrogen, phosphorus, arsenic, antimony, and bismuth, have a maximum positive oxidation state of five in agreement with the presence of five valence electrons. The nitrogen atom, the smallest of the group, shows strong tendencies to add three additional electrons and thus complete the octet; but this property decreases with increasing size so that bismuth forms no stable compounds in which it has a negative oxidation state. Nitrogen and phosphorus are non-metallic in their properties, but the heavier elements of the group are increasingly metallic. Each of the elements forms an acid pentoxide, though the acidic nature of the oxide decreases markedly with increasing size of the positive ions. The elements also form sesquioxides which are acidic with the lighter members, but become basic with the heavier. The elements of the group thus show a complete transition from non-metallic to metallic character.

Nitrogen, like the first member of other groups, differs in many respects from the other elements. For this reason, and also because its importance warrants a more detailed treatment, it will be considered separately. A further discussion of the group properties is given in Paragraph 40.

### NITROGEN

2. **Occurrence.**—Four fifths by volume of the atmosphere is free nitrogen,  $N_2$ . All fertile soils contain the ele-

ment in the form of ammonium salts, nitrates, or nitrites; and nitrogen is a constituent of all proteins. The occurrence of deposits of alkali nitrates has been mentioned (cf. **IV—23**). The amount of nitrogen in the primary rocks is so small that nitrogen ranks among the less abundant elements, constituting but 0.03 per cent of the earth's crust and atmosphere.

**3. Preparation.**—Atmospheric nitrogen is the cheapest source of the element, and large quantities are prepared commercially from the air by fractional liquefaction (cf. **III—6**). This process concentrates the argon somewhat (to about 3 per cent), but the gas is sufficiently pure for most commercial purposes. Nitrogen may, of course, be prepared from the air by the absorption of oxygen by chemical agents, such as heated copper. Pure nitrogen is usually prepared, either by passing ammonia over copper oxide:  $2\text{NH}_3 + 3\text{CuO} = \text{N}_2 + 3\text{H}_2\text{O} + 3\text{Cu}$ , or by heating a solution containing ammonium and nitrite ions:  $\text{NH}_4^+ + \text{NO}_2^- = \text{N}_2 + 2\text{H}_2\text{O}$ . Once the latter reaction is started, it proceeds rapidly or even explosively unless cooled. Other reactions producing nitrogen under appropriate experimental conditions are:  $\text{MnO}_2 + 4\text{NH}_4\text{NO}_3 = \text{Mn}(\text{NO}_3)_2 + 8\text{H}_2\text{O} + 3\text{N}_2$ ;  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 = \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O} + \text{N}_2$ ;  $2\text{P} + 5\text{NH}_4\text{NO}_3 = 2\text{H}_3\text{PO}_4 + 7\text{H}_2\text{O} + 5\text{N}_2$ ;  $\text{CO}(\text{NH}_2)_2 + 2\text{HNO}_2 = \text{CO}_2 + 2\text{N}_2 + 3\text{H}_2\text{O}$ .

**4. Properties of Molecular Nitrogen.**—The more important physical properties of atomic and molecular nitrogen are summarized in Table I. The gas is colorless and tasteless. The low boiling point is indicative of the stability of the molecule. Although the arrangement of the 10 valence electrons in the molecule is not known, the formulae



probably represent the two most important resonating states of the molecule. The molecule is diamagnetic. The



TABLE I  
PHYSICAL AND ATOMIC PROPERTIES OF NITROGEN

Atomic weight.....	14.008	Radius of $M^{-3}$ ion, cm.	
Atomic number.....	7	$\times 10^8$ .....	1.71
Isotopes.....	14, 15	Melting point, °C.....	— 210.0
Electrons in various quantum levels, 1st.....	2	Boiling point, °C.....	— 195.8
2d.....	5	Density of liquid, g./cc.....	0.808
Ionization potentials of gaseous atoms, volts		Heat of vaporization cal. per mole.....	1,350
1st electron.....	14.48	Solubility of $N_2$ at 1 atm. in g. per 100 g. water, 20° C. .	0.00189
2d electron.....	29.47	100° C. .	0.00069
3d electron.....	47.40	Density of gas at 0° C. and 1 atm., g./liter.....	1.2506
4th electron.....	77	Heat of dissociation of $N_2$ in kcal. per mole.....	169.3
5th electron.....	97		

heat of dissociation is probably greater than that of any other diatomic molecule, and is doubtless the chief factor in its very slight reactivity. It may be calculated from thermal data, that at 8,000° C., the gas is only about 40 per cent dissociated into atomic nitrogen. Under the influence of a high voltage discharge, i.e. high velocity electrons, the nitrogen molecule is "activated." Active nitrogen appears to be atomic nitrogen, in which one or more electrons are raised to higher energy levels. Active nitrogen continues to glow for some time after the discharge has been stopped. It combines readily with many elements, phosphorus, sulfur, sodium, etc., with which ordinary nitrogen does not react.

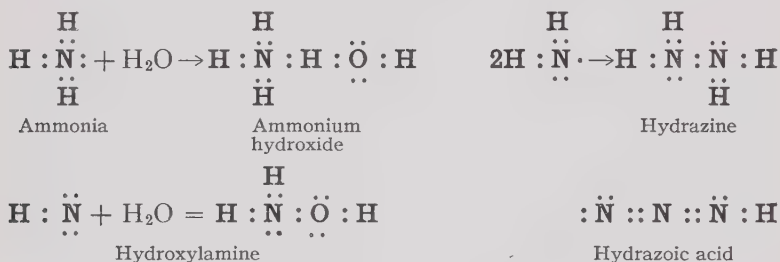
The more important reactions of the element are given in Table II and will be discussed further in connection with the various compounds.

TABLE II  
REACTIONS OF NITROGEN

$N_2 + 3H_2 = 2NH_3$	See ammonia
$N_2 + O_2 = 2NO$	See nitric acid
$N_2 + CaC_2 = CaCN_2 + C$	See cyanamide process
$N_2 + 3Mg = Mg_3N_2$	Also $Li_3N$ , $Ca_3N_2$ , $BN$ , $AlN$ , $TiN$ , etc.
$N_2 + Al_2O_3 + 3C = 2AlN + 3CO$	
$N_2 + 4C + Na_2CO_3 = 2NaCN + 3CO$	See also XIII—24

## COMPOUNDS OF NITROGEN AND HYDROGEN

5. Nitrogen forms with hydrogen compounds in which its oxidation state is  $-3$ ,  $-2$ , and  $-1$ , and a trinitride with an average polar number of  $-1/3$ . The most important of these are the  $-3$  compounds, ammonia and its derivatives. The compound,  $\text{NH}_2$ , exists only in the double molecule,  $\text{N}_2\text{H}_4$ , hydrazine, and the compound  $\text{NH}$  is known only as the hydrate,  $\text{NH}_2\text{OH}$ , hydroxylamine, and its derivatives. The probable electronic structures of these compounds are given below:



The three nitrogen atoms in hydrazoic acid are linear, which corresponds to double bonds between the tetrahedral atoms, but there is probably resonance with other electronic structures.

**6. Manufacture of Ammonia.**—Ammonia was formerly made by the destructive distillation, in the absence of air, of hoofs, horns, and other nitrogenous organic substances; and the solution of the gas was called “spirits of hartshorn.” Coal, due to its vegetable origin, contains nitrogenous matter, and one of the chief sources of ammonia has been the “by-product ammonia,” from coke ovens and coal gas works, in which ammonia produced by the distillation of the coal is separated from the other coal-tar products. The gas is usually washed with water to separate it from the tar, then with sulfuric acid which removes the ammonia as ammonium sulfate. Pure ammonia may be prepared from this by evaporation and treatment with calcium hydroxide.

7. One of the most important industrial developments of recent years has been the **production of synthetic ammonia** through the direct reaction of hydrogen and nitrogen:  $3\text{H}_2 + \text{N}_2 = 2\text{NH}_3$ . The reaction evolves 24,000 cal.; hence, the formation of ammonia is favored by low temperatures, and because of the volume change, by high pressure (cf. Principle of Chatelier, Hildebrand, *Prin. of Chem.*, p. 153), as is indicated in the following table.

TABLE III  
VOLUME PER CENT AMMONIA IN EQUILIBRIUM WITH A 1 TO 3  
MOLAL MIXTURE OF  $\text{N}_2$  AND  $\text{H}_2$

$t^\circ \text{C.}$	ATMOSPHERES				
	30	100	300	600	7000
200.....	67.6	81.5	90.0	95.4	98.3
300.....	30.3	52.0	71.0	84.2	92.5
400.....	10.2	25.1	47.0	65.2	79.9
500.....	3.5	10.6	26.4	42.1	57.5
600.....	1.4	4.2	13.8	23.1	31.4
700.....	0.7	2.2	7.3	12.6	12.9

The rate of reaction is slow at the lower temperatures, and the commercial process has been dependent upon the development of efficient catalysts. The Haber process, developed in Germany, employed according to the original patents, iron oxide containing other metals, such as molybdenum, uranium, or cobalt. Recently developed plants employ, as a catalyst, iron made by the reduction of fused iron oxide (magnetite) containing small amounts of both basic and acidic oxides, such as 0.5 per cent  $\text{Al}_2\text{O}_3$  and 0.5 per cent  $\text{K}_2\text{O}$ ; and operate at pressures of 100–200 atmospheres and temperatures of 550–600° C. The French Claude process attempts to utilize the greater yields at higher pressures by working at 600–1,000 atmospheres. Under these conditions, ordinary sheet iron is very permeable to hydrogen, and the containers must be constructed of special chrome-steel alloys. The world production of syn-

thetic ammonia, in 1938 was about 1,000,000 tons of contained nitrogen as compared to 410,000 tons of by-product ammonia.

8. Another source of ammonia is **calcium cyanamide**,  $\text{CaCN}_2$ , which is formed by the action of nitrogen upon calcium carbide (Table II) at about  $1,200^\circ$ . When treated with steam, cyanamide is hydrolyzed:  $\text{CaCN}_2 + 3\text{H}_2\text{O} = \text{CaCO}_3 + 2\text{NH}_3$ . Much of the cyanamide is used directly as fertilizer. The world production of cyanamide in 1938 was 300,000 tons of contained nitrogen.

9. Attempts have been made to manufacture ammonia commercially by the hydrolysis of aluminum nitride in hot sodium hydroxide solution:  $\text{AlN} + 3\text{H}_2\text{O} = \text{Al(OH)}_3 + \text{NH}_3$ . The nitride is made by heating aluminum oxide and carbon in an atmosphere of nitrogen to about  $1,700^\circ$ . The reaction is slow, and the process is unable to compete with the direct synthesis from the elements. Ammonia may also be prepared by the hydrolysis of sodium cyanide:  $\text{NaCN} + 2\text{H}_2\text{O} = \text{HCOONa} + \text{NH}_3$ .

The historical laboratory method for the preparation of ammonia has been the reaction between an ammonium salt and a strong base (usually calcium hydroxide):  $\text{NH}_4^+ + \text{OH}^- = \text{NH}_3 + \text{H}_2\text{O}$ .

**10. Physical Properties and Uses of Ammonia.**—Ammonia boils at  $-33.4^\circ$ , melts at  $-78^\circ$ , has a critical temperature of about  $133^\circ$ , and a critical pressure of 112 atm. The vapor pressure of the liquid at  $25^\circ$  is 9.90 atm., hence it is easily liquefied by pressure at that temperature. If the pressure upon the liquid is decreased to one atmosphere, the temperature of the liquid, of course, falls to  $-33.4^\circ$ , and the liquid evaporates with the absorption of 330 cal. per g. of ammonia vaporized. This cycle of compression and evaporation is utilized in refrigeration.

The liquid has a density of 0.677 at  $-34^\circ$ , and a dielectric constant of about 20. The specific conductivity at  $-33^\circ$  is about  $10^{-8}$  reciprocal ohms. As a solvent for polar salts,

it resembles water more closely than any other substance, although, due to the lower dielectric constant, salt solutions have a much lower activity (Append. IV). Its unusual solvent action upon the alkali metals has been mentioned (cf. IV—2).

Liquid ammonia is sold under pressure in iron cylinders, and is the most convenient source of the gas. The greater part of the ammonia produced is absorbed in sulfuric acid and sold as fertilizer. Household ammonia, or aqua ammonia, is used in washing and cleaning. Large quantities of ammonia are now oxidized to nitric acid (Par. 32). The most important fields of consumption are given in Table IV.

TABLE IV  
AMMONIA IN U. S. 1938

<i>Production</i>	TONS OF N <sub>2</sub>
Coke ovens.....	150,000
Synthetic.....	190,000
<i>Consumption</i>	
Fertilizer.....	200,000
Manufacture of HNO <sub>3</sub> .....	40,000
Aqua ammonia.....	35,000
Liquid, largely for refrigeration.....	20,000
Salts.....	10,000

**11. Reactions of Ammonia.**—Ammonia does not react readily with air, but in pure oxygen it burns to water and nitrogen:  $4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$ ; 301 kcal. In the presence of platinum as a catalyst, the reaction goes to nitric oxide:  $4\text{NH}_3 + 5\text{O}_2 = 4\text{NO} + 6\text{H}_2\text{O}$ , 215 kcal. This selective oxidation is the basis for the commercial preparation of nitric acid from ammonia (Par. 32). The gas is also oxidized to nitrogen by passing over many heated oxides, e.g. CuO, and by chlorine and bromine (Par. 22). The oxidation of ammonia and ammonium ion in water solutions is discussed in subsequent paragraphs.

Ammonia reacts with water to form ammonium hydroxide (Par. 13). It is absorbed by many salts with the formation of ammoniated compounds similar to solid hy-

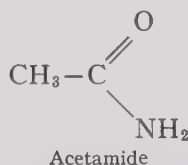
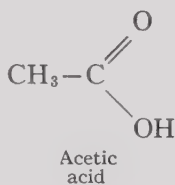
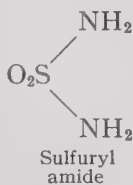
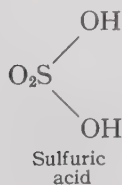
drates, e.g.,  $\text{CaCl}_2 \cdot 2\text{NH}_3$ ,  $\text{CaCl}_2 \cdot 4\text{NH}_3$ . Ammonia forms complex ions with solutions of many metal ions which possess pronounced "coordination" tendencies (cf. VII—2), e.g.,  $\text{Ag}(\text{NH}_3)_2^+$ ,  $\text{Cu}(\text{NH}_3)_4^{++}$ .

Ammonia shows acid properties, in that the three hydrogens are replaceable by metals as illustrated by the following:  $\text{NaNH}_2$ , sodium amide;  $\text{Ag}_2\text{NH}$ , silver imide;  $\text{Li}_3\text{N}$ , lithium nitride. These compounds are formed by heating the metals in ammonia gas:  $2\text{Na} + 2\text{NH}_3 = 2\text{NaNH}_2 + \text{H}_2$ . The acid ionization of ammonia, however, is extremely small, and even sodium amide is completely hydrolyzed in water:  $\text{NaNH}_2 + 2\text{H}_2\text{O} = \text{Na}^+ + \text{OH}^- + \text{NH}_4\text{OH}$ . The amides may be considered as the analogues of the hydroxides of water systems (Table V).

TABLE V  
ANALOGY OF WATER AND AMMONIA SYSTEMS

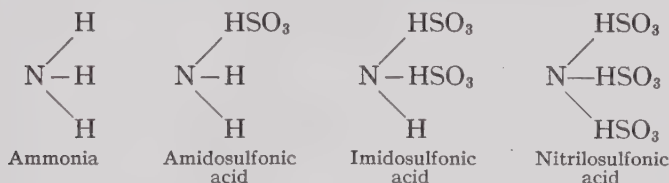
	WATER SYSTEM	AMMONIA SYSTEM
First ionization step.....	$\text{H}^+$ and $\text{OH}^-$ or $\text{OH}_3^+$ and $\text{OH}^-$	$\text{H}^+$ and $\text{NH}_2^-$ or $\text{NH}_4^+$ and $\text{NH}_2^-$
Ionization constant.....	$10^{-14}$ at $25^\circ$	ca. $10^{-18}$ at $-33^\circ$
Base.....	$\text{KOH}$	$\text{KNH}_2$
Acid.....	$\text{HCl}$ ( $\text{OH}_3\text{Cl}$ )	$\text{NH}_4\text{Cl}$
Neutralization reaction.....	$\text{KOH} + (\text{H}_3\text{O})\text{Cl} =$ $\text{KCl} + 2\text{H}_2\text{O}$	$\text{KNH}_2 + \text{NH}_4\text{Cl} =$ $\text{KCl} + 2\text{NH}_3$
Dehydration or deammoniation products of base.....	$\text{K}_2\text{O}$	$\text{K}_2\text{HN}$ and $\text{K}_3\text{N}$
Basic salts.....	$\text{Mg}(\text{OH})\text{Cl}$	$\text{Hg}(\text{NH}_2)\text{Cl}$
Solvates.....	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	$\text{CaCl}_2 \cdot 2\text{NH}_3$

12. Many acids exist, both inorganic and organic, which may be thought of as formed by the replacement of the  $\text{OH}^-$  by  $\text{NH}_2^-$ , e.g.,

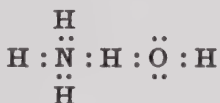




On the other hand, such acids may be considered as compounds in which one or more of the hydrogen atoms of ammonia is replaced by an acid radical, e.g.,



**13. Ammonium Hydroxide.**—Ammonia is extremely soluble in water (1,300 vol. per vol. of  $\text{H}_2\text{O}$  at  $0^\circ$  and 700 vol. at  $20^\circ$ ), forming solutions of ammonium hydroxide,  $\text{NH}_4\text{OH}$ . The hydroxide is a weak base:  $\text{NH}_4\text{OH} = \text{NH}_4^+ + \text{OH}^-$ ,  $K_{25^\circ} = 1.81 \times 10^{-5}$ . A 1*N* solution thus contains 0.0042*N*  $\text{OH}^-$ . To account for the weakness of ammonium hydroxide, it is generally assumed that a hydrogen atom acts as a bond as indicated by the formula:



Values for the specific gravity of aqueous solutions of ammonia are given in Table VI.

TABLE VI  
SPECIFIC GRAVITY OF AQUEOUS AMMONIA AT  $15^\circ \text{C}$ .

SPECIFIC GRAVITY	PER CENT AMMONIA	SPECIFIC GRAVITY	PER CENT AMMONIA
0.998	0.45	0.940	15.63
0.994	1.37	0.930	18.64
0.990	2.31	0.920	21.75
0.980	4.80	0.910	24.99
0.970	7.31	0.900	28.33
0.960	9.91	0.890	31.75
0.950	12.72	0.882	34.95

Water and ammonia react to form solid ammonium hydroxide and the **oxide**,  $(\text{NH}_4)_2\text{O}$ , at  $-79^\circ$ . These pure com-

pounds decompose upon heating, so only the water solutions of ammonium hydroxide are known at room temperature.

**14. Ammonium Amalgam.**—The free ammonium radical,  $\text{NH}_4$ , may be prepared as an amalgam by the reduction of ammonium ion in the presence of mercury:  $\text{NH}_4^+ + e^- = \text{NH}_4$ . The reduction may be accomplished electrolytically, using a solution of ammonium sulfate and a mercury cathode, or by the action of sodium amalgam upon an ammonium solution. At ordinary temperature, the radical is unstable, decomposing into ammonia and hydrogen, and the amalgam is a spongy mass, due to the bubbles of gas, but at low temperatures the amalgam is a hard, stable substance. In forming an amalgam, the ammonium radical thus appears to possess distinctly metallic properties.

**15. Ammonium Salts.**—Ammonium ion resembles thal-  
lous and potassium ions in the solubility and crystalline form of its salts. The four hydrogen atoms are arranged in tetrahedral form about the nitrogen, and the approximate diameter of the ion in crystals is  $1.50 \times 10^{-8}$  cm. Two points of dissimilarity from thal-  
lous and potassium ions are the weakness of ammonium hydroxide, and the volatility of ammonium salts. All ammonium salts volatilize at temperatures around  $300^\circ$ , except compounds, such as the nitrate and dichromate, which decompose with the oxidation of the ammonia. The vapor of the sublimed salt is largely dissociated into ammonia and the acid, e.g.  $\text{NH}_4\text{Cl}(\text{s}) = \text{NH}_3(\text{gas}) + \text{HCl}(\text{gas})$ . In fact, it is this dissociation taking place on the crystal surface which is probably responsible for the ready volatility of the salt. Ammonium salts are highly ionized, and slightly acid by hydrolysis. The constant for the hydrolysis,  $K = (\text{NH}_4\text{OH})(\text{H}^+)/(\text{NH}_4^+)$ , is  $5.5 \times 10^{-10}$  at  $25^\circ \text{C}$ . A  $1N \text{NH}_4^+$  solution thus contains  $2.3 \times 10^{-5}N \text{H}^+$ .

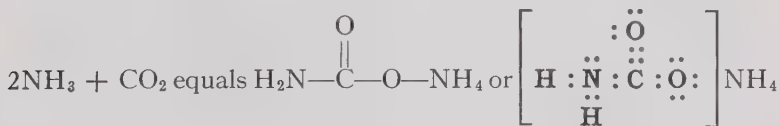
**16. Ammonium chloride** is made by absorbing ammonia in hydrochloric acid. It crystallizes from solution in feathery crystals of the regular system, having the same type of

crystal lattice as cesium chloride, but changing at higher temperatures into the sodium chloride lattice. The vapor pressure of the solid reaches one atmosphere at 338° C. The salt is used in "galvanizing" iron, and in soldering, to clean metal surfaces of oxides, the action being due to the presence of free hydrochloric acid in the vapor. It is also used in "dry" batteries (cf. XVIII—9), and in textile dyeing. Its common name is sal ammoniac.

**Ammonium bromide** and **iodide** are similar to the chloride.

The **nitrate** exists in five crystalline modifications between the temperatures of  $-20^{\circ}$  and  $125^{\circ}$ . When heated gently, it decomposes into nitrous oxide and water. The compound is really a high explosive, but is extremely difficult to detonate. It is, however, employed extensively as an explosive mixed with trinitrotoluene under the name of amatol.

**17. Ammonium carbonate** solutions are highly hydrolyzed, and lose ammonia to form the bicarbonate:  $2\text{NH}_4^+ + \text{CO}_3^{--} = \text{NH}_4^+ + \text{HCO}_3^- + \text{NH}_3$ . The so-called solid ammonium carbonate is a mixture of the bicarbonate and **ammonium carbamate**, and is made by heating a mixture of the ammonium sulfate and calcium carbonate in iron retorts. It may also be formed by the reaction of ammonia and carbon dioxide.



Upon heating, ammonium carbamate loses water to form **urea**:  $\text{NH}_4\text{CO}_2\text{NH}_2 = \text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O}$ .

**Ammonium sulfate**, prepared by passing "by-product" ammonia into sulfuric acid, has been the principal source of ammonium compounds. Synthetic ammonia has, however, now become the greatest potential source of am-

monium compounds. The sulfate is employed extensively as a fertilizer, but if a cheaper method of preparing phosphoric acid from phosphate rock can be developed, the sulfate will doubtless be replaced by the **phosphate**, as the absorption of ammonia in this acid will serve to eliminate the cost of the sulfuric acid and at the same time give a compound, both constituents of which are valuable fertilizers.

**Ammonium sulfide**,  $(\text{NH}_4)_2\text{S}$ , solutions, made by passing hydrogen sulfide into ammonium hydroxide, are largely hydrolyzed to the bisulfide,  $\text{NH}_4\text{HS}$ . The use of these solutions is frequently referred to in connection with the precipitation of metal sulfides in qualitative analyses. The sulfide readily absorbs sulfur forming polysulfides (cf. **XI—26**). The polysulfide also forms through the action of the oxygen of the air upon solutions of the sulfide.

**Ammonium thiocyanate**,  $\text{NH}_4\text{SCN}$ , is used in dyeing to prevent injurious action of iron salts upon the color (see  $\text{Fe}(\text{SCN})_3$ ). It is sometimes prepared by the reaction of ammonia and carbon disulfide:  $\text{CS}_2 + 2\text{NH}_3 = \text{NH}_4\text{SCN} + \text{H}_2\text{S}$ . Ammonium **dithiocarbamate**,  $\text{NH}_4\text{S}_2\text{CNH}_2$ , forms as an intermediate compound.

**Ammonium peroxysulfate**,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , formed by the electrolysis of a concentrated solution of the acid sulfate, is an important oxidizing agent.

**18. Analytical.**—The perchlorate, cobaltinitrite, chloroplatinate, and acid tartrate, may be precipitated similarly to the potassium salts; but a more delicate test for ammonium compounds is the formation of ammonium hydroxide upon the addition of a strong base and the subsequent volatilization of ammonia gas:  $\text{NH}_4^+ + \text{OH}^- = \text{NH}_4\text{OH}$  and  $\text{NH}_4\text{OH} = \text{NH}_3 + \text{H}_2\text{O}$ . The ammonia is detected by its odor, or by its action upon moistened red litmus paper placed over the solution. Quantitatively, ammonium salts are determined by treating the sample with excess sodium hydroxide, and distilling the ammonia into a known volume

of standard acid. The excess acid is then titrated with standard base, using methyl orange as an indicator. Small amounts of ammonia are determined by means of Nessler's reagent (cf. VIII—25).

**19. Hydrazine.**—Ammonium salts may be oxidized electrolytically to hydrazine, if certain viscous substances, such as glue or starch are added to the electrolyte. Hydrazine is usually prepared by treating dilute ammonia (in the presence of glue, etc.) with chlorine to form the monochloramine,  $\text{NH}_2\text{Cl}$ ; and then adding an excess of ammonia:  $2\text{NH}_3 + \text{Cl}_2 = \text{NH}_2\text{Cl} + \text{NH}_4\text{Cl}$ , and  $2\text{NH}_3 + \text{NH}_2\text{Cl} = \text{N}_2\text{H}_4 + \text{NH}_4\text{Cl}$ . The sulfate,  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ , or  $(\text{N}_2\text{H}_5)_2\text{SO}_4$ , is not very soluble, and hydrazine is readily purified by crystallization as such. It may also be prepared by the reduction of the potassium sulfite-nitric oxide complex,  $\text{K}_2\text{SO}_3 \cdot 2\text{NO}$ , with sodium amalgam, and by the reduction of a number of organic nitrogen compounds. With water hydrazine forms the weak base,  $\text{N}_2\text{H}_5\text{OH}$ , which gives in acid solution the ion,  $\text{N}_2\text{H}_5^+$ . For the dissociation,  $\text{N}_2\text{H}_4 + \text{H}_2\text{O} = \text{N}_2\text{H}_5^+ + \text{OH}^-$ , the value for  $K$  is  $8.5 \times 10^{-7}$ . The pure substance may be prepared as a fuming liquid by distilling hydrazine hydrate with barium oxide:  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} + \text{BaO} = \text{N}_2\text{H}_4 + \text{Ba}(\text{OH})_2$ . The liquid boils at  $113.5^\circ$  without decomposition. Hydrazine is a good reducing agent even in acid solution. It is oxidized quantitatively to nitrogen by iodate, chlorine, bromine, and iodine. The alkaline solution is readily oxidized by oxygen. Many oxidizing agents which gain one electron per molecule react with hydrazine to form both nitrogen and ammonia:  $\text{N}_2\text{H}_5^+ + \text{Fe}^{+++} = \text{Fe}^{++} + \frac{1}{2}\text{N}_2 + \text{NH}_4^+ + \text{H}^+$ . Hydrazine reacts with nitrous acid to form hydrazoic acid (Par. 21). Hydrazine is not easily reduced to ammonia. The relation of hydrazine to ammonia is analogous to that of hydrogen peroxide to water.

**20. Hydroxylamine.**—Hydroxylamine,  $\text{NH}_2\text{OH}$ , is best prepared by the reduction of 1 mole of nitrous acid with

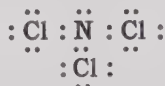
2 moles of sulfurous acid (Par. 30). The reduction is carried out at  $0^\circ$  in neutral solution ( $\text{NaHSO}_3$ ) and forms first the ion of hydroxylaminedisulfonic acid:  $\text{NO}_2^- + \text{SO}_2 + \text{HSO}_3^- = \text{NOH}(\text{SO}_3)_2^{--}$ . This is then hydrolyzed by heating in acid solution:  $\text{NOH}(\text{SO}_3)_2^{--} + 2\text{H}_2\text{O} = \text{H}_3\text{NOH}^+ + \text{H}^+ + 2\text{SO}_4^{--}$ . Hydroxylamine is also obtained by the reduction of nitric and nitrous acid in dilute solution, by strong reducing agents such as tin, and zinc. The electrolytic reduction of nitric acid with most metal electrodes yields ammonia, but with a mercury cathode, hydroxylamine is formed. Hydroxylamine in solutions of acids forms the ion,  $\text{NH}_3\text{OH}^+$ , and upon evaporation of the solution, salts such as  $\text{NH}_3\text{OH}\cdot\text{Cl}$ , are obtained.  $\text{NH}_2\text{OH} + \text{H}_2\text{O} = \text{NH}_3\text{OH}^+ + \text{OH}^-$ ,  $K = 6.6 \times 10^{-9}$ . The anhydrous compound may be prepared by distilling, under reduced pressure, an alcoholic solution of the hydrochloride with sodium methylate:  $\text{NH}_3\text{OH}\cdot\text{Cl} + \text{CH}_3\text{ONa} = \text{NH}_2\text{OH} + \text{CH}_3\text{OH} + \text{NaCl}$ . The melting point is  $33^\circ$ , and at  $57^\circ$ , the vapor pressure is 22 mm. At higher temperatures the liquid is very explosive. Ferric ion (in excess) in acid solution oxidizes hydroxylamine quantitatively to nitrous oxide, and more powerful oxidizing agents give nitrate. If the  $\text{H}^+$  is low and  $\text{NH}_2\text{OH}$  is in excess, nitrogen is largely formed. Hydroxylamine is reduced by moderately powerful reducing agents, such as ferrous hydroxide, or zinc in acid solution. Aqueous solutions, especially if alkaline, decompose forming ammonia and nitrogen, or nitrous oxide.

**21. Hydrazoic Acid.**—Nitrous oxide reacts with sodamide at  $200^\circ$  to form sodium azide:  $\text{N}_2\text{O} + \text{H}_2\text{NNa} = \text{NaN}_3 + \text{H}_2\text{O}$ . Hydrazine and its derivatives react in the cold with nitrous acid or trichloronitride to form hydrazoic acid:  $\text{N}_2\text{H}_4 + \text{O}_2\text{NH} = \text{HN}_3 + 2\text{H}_2\text{O}$ . Hydrazoic acid is a somewhat stronger acid than acetic acid,  $K = 4.5 \times 10^{-4}$ , and the ion,  $\text{N}_3^-$ , resembles chloride ion in the solubility of its salts and in its reversible reaction with hypochlorous acid:  $\text{HClO} + \text{HN}_3 \rightleftharpoons \text{ClN}_3 + \text{H}_2\text{O}$ .



The product, chlorazide, like chlorine, is a gas, but is highly explosive. The iodo-azide also exists. Sodium azide tastes like sodium chloride, and is highly poisonous. The free acid boils at  $37^\circ$ , but the warm liquid is violently explosive, as the compound is highly endothermic (62 kcal.). The acid is both a powerful oxidizing agent and a powerful reducing agent.  $\text{NH}_4^+ + \text{N}_2 = \text{HN}_3 + 3\text{H}^+ + 2e^-$ , -1.82 volts and  $\text{HN}_3 = \frac{3}{2}\text{N}_2 + \text{H}^+ + e^-$ , 2.8 volts. The acid reacts quantitatively with ceric ion:  $2\text{Ce}^{++++} + 2\text{HN}_3 = 3\text{N}_2 + 2\text{Ce}^{+++} + 2\text{H}^+$ . The crystal structure of the azides from X-ray data show that the three nitrogen atoms are in line, with a distance between the atomic centers of  $1.16 \times 10^{-8}$  cm. Lead azide is now used extensively in the manufacture of percussion caps.

**22. Halogen Nitrides.**—Trichlornitride, also called nitrogen trichloride,  $\text{Cl}_3\text{N}$ , is formed almost quantitatively by the action of excess chlorine or hypochlorous acid with ammonium ion in excess of strong acid:  $\text{NH}_4^+ + 3\text{Cl}_2 = \text{Cl}_3\text{N} + 4\text{H}^+ + 3\text{Cl}^-$ , and  $\text{NH}_4^+ + 3\text{HClO} = \text{Cl}_3\text{N} + \text{H}^+ + 3\text{H}_2\text{O}$ . With low concentration of hydrogen ion, nitrogen is evolved, probably through the reaction:  $\text{NCl}_3 + \text{NH}_4^+ = \text{N}_2 + 4\text{H}^+ + 3\text{Cl}^-$ . With dilute equimolal solutions of ammonia and hypochlorite, **chloramine** is formed:  $\text{NH}_3 + \text{ClO}^- = \text{NH}_2\text{Cl} + \text{OH}^-$ . Both substances are highly explosive, oily liquids, and are partially hydrolyzed by water to ammonia and hypochlorous acid. Because of this type of hydrolysis and the method of preparation, the nitrogen is often considered as being in the -3 oxidation state but the classification is not very significant in view of the non-polar character of the bonds between the nitrogen and chlorine.



Trichlornitride



Chloramine

Iodine reacts with ammonia, forming a dark brown solid,

the so-called **nitrogen triiodide**,  $I_3N \cdot NH_3$ . When dry, it explodes with the slightest touch. It may also be prepared by the addition of iodine chloride in concentrated hydrochloric acid to an excess of concentrated ammonia. The formation of ammonium hypoiodite,  $NH_4IO$ , appears to be an intermediate step. Bromine reacts with ammonia to liberate nitrogen, and the reaction is frequently employed to remove bromine from a solution. **Nitrogen trifluoride** has been prepared by the electrolysis of anhydrous ammonium fluoride,  $NH_4HF_2$ . It is more stable than the trichloride. The **trioxyfluoride**,  $NO_3F$ , forms by the action of fluorine upon pure nitric acid. The fluorine atom is bonded to one of the oxygen atoms.

**23. Nitrogen and Sulfur.**—Sulfur nitride,  $S_4N_4$ , may be prepared by the action of liquid ammonia upon sulfur, or by the action of ammonia on sulfur chloride in benzene. The compound is orange-red and may be sublimed under reduced pressure at  $100^\circ$ , but explodes at higher temperatures. It hydrolyzes in water to form ammonia, sulfurous, and thiosulfuric acids. The highly explosive compounds  $(Se_4N_4)_x$  and  $Te_3N_4$  have been prepared.

## OXIDES AND ACIDS OF NITROGEN

**24.** Nitrogen forms oxides, in which it possesses the oxidation states  $+1$  to  $+5$ , inclusive, and acids corresponding to the  $+1$ ,  $+3$ , and  $+5$  states. In addition, there is a nitrogen peroxide, and a peroxyacid, but these are relatively unimportant. Electronic formulae are given below. These must not be interpreted as representing the actual position of the electrons, but simply as a representation of the total number of electrons and a distribution which appears to be in harmony with the known facts relating to the various compounds. In molecules which do not have completed octets of electrons for all of the atoms, there doubtless is resonance of electrons between atoms with completed octets and those with incomplete octets. The relative positions of

the atoms in the molecule are known, in a majority of cases, from X-ray data on the solid crystals.



Nitrous oxide (+ 1)



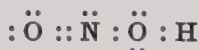
Hyponitrous acid (+ 1)



Nitric oxide (+ 2)



Nitrous anhydride (+ 3)



Nitrous acid (+ 3)



Nitrogen dioxide (+ 4)



Nitrogen tetroxide (+ 4)



Nitric anhydride (+ 5)



Nitric acid (+ 5)

**25. Nitrous Oxide.**—Nitrous oxide is prepared commercially by the decomposition of ammonium nitrate through gentle heating:  $\text{NH}_4\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$ . The reaction must be carefully controlled, as overheating may result in the explosive decomposition into nitrogen, oxygen, and water. The oxide is also a product of various other reactions, including:  $\text{NH}_3\text{OH}\cdot\text{NO}_2 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$ ;  $\text{HN}_3 + \text{HNO}_2 = \text{N}_2 + \text{N}_2\text{O} + \text{H}_2\text{O}$ ;  $\text{N}_2\text{H}_4\cdot\text{HNO}_2 = \text{N}_2\text{O} + \text{NH}_3 + \text{H}_2\text{O}$ . The oxide is a colorless gas which may be liquefied by a pressure of 50 atmospheres at  $20^\circ$ . The critical temperature is  $35^\circ$ . It is soluble to the extent of 1.3 per vol. of water at  $20^\circ$ , and at low temperatures forms a hydrate,  $\text{N}_2\text{O}\cdot 6\text{H}_2\text{O}$ . Crystal structure data of the solid

show all three atoms of the molecule to be in a line, with the oxygen on one end.

The heat of formation of nitrous oxide is negative, about 19.7 kcal. per mole; and the gas is unstable in respect to the decomposition into its elements. However, the rate of decomposition is not appreciable at ordinary temperatures. A glowing splinter bursts into flame in nitrous oxide, and phosphorus and sulfur burn readily, nitrogen being liberated in the reaction. Strong oxidizing agents, such as permanganate, oxidize nitrous oxide to nitric oxide. Metals do not tarnish readily in nitrous oxide, and it does not combine with nitric oxide as does oxygen. The gas is employed extensively as an anaesthetic. Inhaled in small amounts, it often produces a type of hysteria, hence its common name "laughing gas." The pure liquid oxide is put on the market in heavy steel containers.

**26. Hyponitrous Acid.**—Hydroxylamine is oxidized by mercuric oxide or nitrous acid to hyponitrous acid:  $2\text{NH}_2\text{OH} + 2\text{HgO} = \text{H}_2\text{N}_2\text{O}_2 + 2\text{Hg} + 2\text{H}_2\text{O}$ ;  $\text{NH}_2\text{OH} + \text{HNO}_2 = \text{H}_2\text{N}_2\text{O}_2 + \text{H}_2\text{O}$ . The ion is also formed by the reduction of nitrite with sodium amalgam or electrolytically with a mercury cathode. The silver salt,  $\text{Ag}_2\text{N}_2\text{O}_2$ , is slightly soluble, and the free acid may be formed by treating the silver salt with an ether solution of hydrogen chloride. Upon evaporation of the ether, the acid is obtained as a highly explosive solid. In water solution the acid slowly decomposes into nitrous oxide and water:  $\text{H}_2\text{N}_2\text{O}_2 = \text{H}_2\text{O} + \text{N}_2\text{O}$ . The reaction is not reversible. The double formula is assigned from measurements of the molecular weight in various solvents. The following potentials relate hyponitrous acid to nitrous acid and hydroxylamine,  $2\text{H}_2\text{O} + \text{H}_2\text{N}_2\text{O}_2 = 2\text{HNO}_2 + 4\text{H}^+ + 4e^-$ ,  $-0.80$  volt, and  $2\text{NH}_3\text{OH}^+ = \text{H}_2\text{N}_2\text{O}_2 + 6\text{H}^+ + 4e^-$ ,  $-0.44$  volt. The ionization constants of  $\text{H}_2\text{N}_2\text{O}_2$  are  $K_1 = 9 \times 10^{-8}$  and  $K_2 = 1 \times 10^{-11}$ .

The compound, **nitroxyl**,  $\text{NOH}$ , appears to be formed as

an intermediate step in the oxidation of hydroxylamine or the reduction of nitrous acid. Under various conditions it may react to give  $N_2O$  or  $H_2N_2O_2$  or it may react with excess hydroxylamine to give nitrogen,  $NH_2OH + NOH = N_2 + H_2O$ . By its reaction with excess of nitrous acid nitric oxide may be formed. Sodium reacts with nitric oxide at low temperatures to form  $NaNO$ , which may be considered to be a salt of  $NOH$ . The sodium compound liberates  $N_2O$  with water.

**27. Nitric Oxide.**—Pure nitric oxide is formed by the addition of dilute nitric acid (sp. gr. 1.2) to a boiling solution of ferrous sulfate and dilute sulfuric acid:  $3Fe^{++} + 4H^+ + NO_3^- = 3Fe^{+++} + NO + 2H_2O$ . It may also be formed by the reduction of dilute nitric acid by various metals, such as copper or silver, although usually contaminated by some nitrogen, nitrous oxide, or nitrogen dioxide.

Nitric oxide is highly endothermic, but is the most stable of the nitrogen oxides at high temperatures. It is formed to a small per cent in a mixture of nitrogen and oxygen in an electric arc, the reaction being the basis for the various arc processes for the fixation of nitrogen (see Nitric Acid). The oxide is also an intermediate step in another important process for the manufacture of nitric acid, namely, the oxidation of ammonia (Par. 32).

Nitric oxide resembles nitrogen and oxygen in physical properties. The critical temperature is  $-93^\circ$ , and the boiling point  $-150.2^\circ$ . The heat of dissociation into  $N_2$  and  $O_2$  is  $-21$  kcal., and into atomic nitrogen and oxygen about  $-150$  kcal. It is doubtless this latter large heat that renders the rate of decomposition so slow at low temperatures. The molecule contains an odd number of valence electrons, but possesses only slightly the general tendency of such compounds to form double molecules, nor is it colored. In the liquid state, however, it appears to be about 90 per cent associated into  $(NO)_2$ . The oxide is magnetic, its magnetic susceptibility being approximately

half that of oxygen, which contains two unpaired electrons (cf. III—3).

At ordinary temperatures, nitric oxide reacts with oxygen or air to form brown nitrogen dioxide; but the equilibrium is reversed at higher temperatures (Table VII):  $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$ . Vigorously burning wood or phosphorus continues to burn in nitric oxide, but it does not support the combustion of more feebly burning substances, such as sulfur or a tallow candle. The oxide is somewhat soluble in water, 4.7 vol. per 100 vol. of water at  $20^\circ$  and 1 atm. It is, however, very soluble in solutions of ferrous salts due to the formation of the dark brown colored complex ion,  $\text{FeNO}^{++}$  (cf. Par. 39). Complex ions with cupric, cobaltous, and platinous also exist, as well as the complex sulfite,  $\text{K}_2\text{SO}_3 \cdot 2\text{NO}$ .

**28. Nitrogen Sesquioxide, and Di- or Tetra-oxide.**—The sesquioxide,  $\text{N}_2\text{O}_3$ , is the anhydride of nitrous acid:  $\text{N}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{HNO}_2$ . The acid is very unstable and readily evolves the oxide, or, more correctly, a mixture of nitric oxide and nitrogen dioxide, since the sesquioxide is itself unstable at ordinary temperatures:  $\text{N}_2\text{O}_3 = \text{NO} + \text{NO}_2$ . The equimolal mixture of oxides may be condensed to a dark blue liquid boiling at  $3.5^\circ$ . If the liquid is completely dried, it may be vaporized without dissociation.

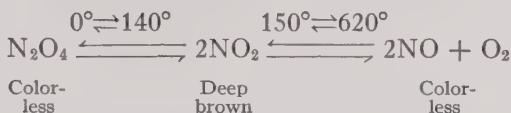
The dioxide,  $\text{NO}_2$  (also incorrectly called peroxide), is largely polymerized in the liquid to tetroxide,  $\text{N}_2\text{O}_4$ . At the boiling point,  $21.3^\circ$ , the gaseous tetroxide is only about 20 per cent dissociated into the dioxide, but at  $135^\circ$  the dissociation is 99 per cent. Above  $150^\circ$ , the dioxide begins to dissociate into nitric oxide and oxygen.

TABLE VII  
DISSOCIATION OF NITROGEN DIOXIDE

$t^\circ \text{C.}$ . . . . .	130	185	350	500	620
Per cent dissociated. . . . .	0	5	20	57	100



The dioxide is an "odd molecule," and like the majority of such molecules, in addition to its tendency to polymerize, it is colored, the color in this case being a deep red-brown. The pure tetroxide, however, is colorless, and upon heating, therefore, undergoes a striking color change.



29. These oxides are involved in three important equilibria with water, nitric, and nitrous acids: (1) In small concentrations, nitrogen dioxide reacts with water in the cold to give a blue solution of nitric and nitrous acids:  $2\text{NO}_2 + \text{H}_2\text{O} = \text{HNO}_2 + \text{H}^+ + \text{NO}_3^-$ ,  $K = 10^5$ . It follows from the equilibrium constant that in a dilute solution of the two acids the concentration of nitrogen dioxide is very small. (2) Nitrous acid is unstable in respect to the decomposition:  $3\text{HNO}_2 = \text{H}^+ + \text{NO}_3^- + 2\text{NO} + \text{H}_2\text{O}$ ,  $K = 30$ . This equilibrium is comparatively slow in cold dilute solutions, and, from the value of the constant, is rather easily reversed. (3) In warm concentrated solutions of nitric acid, the quantity of nitrous acid, which may be present, is very small, and the principal equilibrium is the following:  $3\text{NO}_2 + \text{H}_2\text{O} = 2\text{NO}_3^- + 2\text{H}^+ + \text{NO}$ ,  $K = 2 \times 10^8$ . Although the equilibrium constant favors largely the formation of nitric acid from the dioxide, concentrated nitric acid may, however, be reduced by nitric oxide. The third reaction is extremely important in connection with synthetic nitric acid processes (Par. 32). With alkaline solutions only reaction (1) occurs, i.e. nitrate and nitrite are formed and the equimolal mixture of NO and  $\text{NO}_2$  gives almost pure nitrite.

It follows from these equilibria that the concentration of nitric acid affects greatly the reduction products of the acid. This concentration effect is illustrated by the following sum-

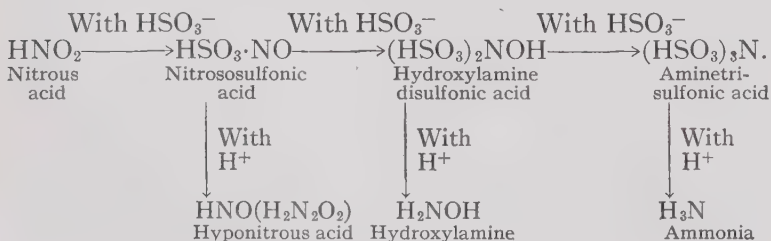
mary of the products formed by the action of nitric acid upon arsenous oxide:

DENSITY OF HNO <sub>3</sub>	1.20	1.25	1.35	1.45
Product . . . . .	Almost pure NO	Mostly NO, a little NO <sub>2</sub>	Equimolal mixture, NO, NO <sub>2</sub>	1 part NO, 10 parts NO <sub>2</sub>

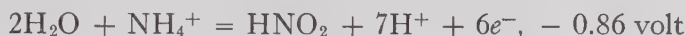
**30. Nitrous Acid and Nitrites.**—The formation of nitrous acid, HNO<sub>2</sub>, from the dioxide or sesquioxide has been discussed above. A solution containing nitrous acid may also be formed by the hydrolysis in dilute acid of nitrosylsulfuric acid:  $\text{NO}_2\text{HSO}_3 + \text{H}_2\text{O} = 2\text{H}^+ + \text{SO}_4^{--} + \text{HNO}_2$ . A solution of nitrous acid is conveniently formed by the addition of sulfuric acid to a nitrite in the cold. Nitrous acid is weak, the dissociation constant being  $4.5 \times 10^{-4}$ . The solution has a slight bluish color. The decomposition of the water solution has been discussed (Par. 29). Nitrous acid is a rapid and fairly strong oxidizing agent:



It thus oxidizes iodide quantitatively to iodine. Certain strong reducing agents, e.g., stannous ion, are able to reduce nitrous acid to the negative oxidation states, but with many equally strong reducing agents, e.g., titanous ion, the reduction stops at NO. In general, such reductions involve a number of steps, but only in the case of sulfurous acid has the mechanism been worked out.



The reactions indicated on the horizontal are reversed in strong alkali. The reduction products may be hydrolyzed in acid solution to form the compounds indicated by the vertical arrows. The reduction potential of nitrous acid to ammonium ion is:



and in alkaline solution:



Nitrous acid may also act as a reducing agent:



A strong oxidizing agent is thus required, but the reaction is quantitative with permanganate.

Nitrites are usually prepared by heating the alkali nitrates either alone,  $2\text{KNO}_3 = 2\text{KNO}_2 + \text{O}_2$ , or with carbon or lead, to decrease the temperature of conversion:  $2\text{KNO}_3 + \text{C} = 2\text{KNO}_2 + \text{CO}_2$ .

Nitrite forms complex ions with many positive ions, including cobaltic, ferrous, chromic, cupric, platinous; the most important being that with cobaltic ion,  $\text{Co}(\text{NO}_2)_6^{---}$ . The alkali nitrites are extremely soluble, but the silver nitrite is but slightly soluble. The silver salt in contact with solution decomposes upon heating, according to the equation:  $2\text{AgNO}_2 = \text{Ag} + \text{NO} + \text{Ag}^+ + \text{NO}_3^-$ .

Nitrous acid reacts with ammonia and with organic primary amines to form nitrogen:  $\text{NH}_3 + \text{HNO}_2(\text{NH}_4^+ + \text{NO}_2^-) = \text{N}_2 + 2\text{H}_2\text{O}$ ;  $\text{RNH}_2 + \text{HNO}_2 = \text{N}_2 + \text{ROH} + \text{H}_2\text{O}$ ;  $\text{CO}(\text{NH}_2)_2 + 2\text{HNO}_2 = 2\text{N}_2 + \text{CO}_2 + 3\text{H}_2\text{O}$ . The reaction with urea,  $\text{CO}(\text{NH}_2)_2$ , is often employed to remove nitrites from solution. Nitrous acid forms nitrosoamines with secondary amines:  $\text{R}_2\text{NH} + \text{HNO}_2 = \text{R}_2\text{N}\cdot\text{NO} + \text{H}_2\text{O}$ . With aniline hydrochloride in the cold, nitrous acid forms diazonium chloride:  $\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HCl} + \text{HNO}_2 = \text{C}_6\text{H}_5\text{N}_2\text{Cl} + 2\text{H}_2\text{O}$ . This reaction is important in the

synthesis of many organic compounds. Due to the weakness of nitrous acid, soluble nitrites are slightly hydrolyzed. Nitrites are readily distinguished from nitrates by the fact that ferrous ion is oxidized in dilute acid (acetic) by nitrite, but not by nitrate, to give (with excess of the ferrous ion) the characteristic brown color of the  $\text{Fe}(\text{NO})^{++}$  ion. Nitrites are quite poisonous.

**31. Nitric Acid.**—Pure nitric acid is a colorless liquid, density 1.54, freezing point  $-47^\circ$ , boiling point  $86^\circ$  under atmospheric pressure, and  $35^\circ$  under pressure of 20 mm. The concentrated acid is usually colored yellow, due to the presence of a percentage of the dioxide formed by the slow decomposition:  $4\text{HNO}_3 = 4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2$ . The speed of the decomposition is increased by higher temperature and by light. The acid fumes strongly in moist air; the water solution has a constant boiling mixture of 68 per cent acid, density 1.41, and boiling point of  $120.5^\circ$ . Upon repeated distillation of the pure acid, the constant boiling mixture is obtained through the formation of water by the decomposition reaction.

The **anhydride or pentoxide** may be formed by the action of phosphorus pentoxide upon concentrated nitric acid:  $2\text{HNO}_3 + \text{P}_2\text{O}_5 = \text{N}_2\text{O}_5 + 2\text{HPO}_3$ . It is a white solid which readily sublimes, and is easily decomposed into the dioxide and oxygen. The freezing point composition curves for the acid and water show the existence of mono-, di-, and tri-hydrates at low temperatures. Water solutions of nitric acid are highly ionized (Append. IV).

**32.** Three processes for the **manufacture of nitric acid** are now in use: (1) the older process of preparation from Chile saltpeter and sulfuric acid, (2) from nitric oxide formed by the oxidation of ammonia, (3) from nitric oxide formed by the direct union of the elements.

For many years, Chile saltpeter (cf. **IV—23**) was practically the only source of nitric acid. The acid is produced from the salt by heating with concentrated sulfuric acid:

$\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{HNO}_3 + \text{NaHSO}_4$ . The reaction proceeds because of the greater volatility of nitric acid, and is carried out under reduced pressure in order to operate at the lowest possible temperature, and thus keep down the decomposition of the acid. The reaction mixture is heated in iron retorts, and nitric acid condensed and collected in glass tubes and vessels. The sodium acid sulfate is valuable because of its acid properties, and is used in various industries.

Since it is now possible to make ammonia synthetically at as low a cost per pound of nitrogen as Chile nitrate can be mined and extracted, ammonia has become the principal commercial source of the acid. In 1938 the production of nitric acid in the United States was approximately 160,000 tons from ammonia and only 20,000 tons from nitre. The oxidation is carried out by passing a mixture of ammonia (about 10 per cent) and air over a heated platinum gauze:  $4\text{NH}_3 + 5\text{O}_2 = 4\text{NO} + 6\text{H}_2\text{O}$ . The platinum gauze is maintained at a temperature of 900–1000° C. The gaseous mixture is heated to about 300° before entering the catalyst, and the heat of oxidation is sufficient to maintain the catalyst at the high temperature once the reaction is started. The efficiency of oxidation is about 96 per cent of the ammonia. The gas from the catalyst passes into absorption towers:  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$  and  $3\text{NO}_2 + \text{H}_2\text{O} = 2\text{HNO}_3 + \text{NO}$ . The first of these reactions is rather slow, but is catalyzed by most surfaces. The second reaction has been discussed at length under the oxide. The final two or three per cent of the oxide is absorbed in sodium carbonate solution to give a mixture of nitrate and nitrite. An important factor in the successful development of the process has been the use of chrome-steel alloys in the absorption towers, as this metal is practically unattacked by nitric acid.

**33.** Synthesis of nitric acid from its elements can only be carried out at extremely high temperatures as indicated in Table VIII.

TABLE VIII  
EQUILIBRIUM IN THE REACTION  $\text{N}_2 + \text{O}_2 = 2\text{NO}$

$t^\circ \text{C}.$ .....	1227	1727	2227	2627	2927	3927
Per cent of $\text{N}_2 + \text{O}_2$ combined..	0.1	0.6	1.8	3.2	4.2	10.0

The existence of nitric oxide at ordinary temperatures is obviously due to a very slow rate of decomposition, and this rate becomes rapid only at high temperatures.

TABLE IX  
ESTIMATED TIME REQUIRED FOR HALF DECOMPOSITION OF NO

$t^\circ \text{C}.$ .....	721	1227	1627	1827	2627
Time.....	81.6 years	1.3 days	2.1 mm.	5.1 sec.	$3 \times 10^{-5}$ sec.

A process for the direct synthesis of nitric oxide must, then, involve the heating of a mixture of oxygen and nitrogen to about  $2000^\circ \text{C}.$ , followed by the rapid cooling of the equilibrium mixture. This is carried out commercially (chiefly in Norway) by blowing the gases through an electric arc. The gases pass through the arc and are cooled rapidly by coming in contact with the walls of the tube. The nitric oxide is absorbed as discussed above in the ammonia process. Under the best working conditions, the yield of nitric oxide is only about 2.5 per cent, and it is doubtful if the process can continue to compete with nitric acid from ammonia, even in countries where electrical power is very cheap. The yield is somewhat greater than is to be expected from the equilibrium values, doubtless due to the direct absorption of electrical energy by nitrogen to form activated molecules. The process occurs in nature through the action of lightning, and the annual fixation of nitrogen during thunder storms is doubtless very large.

**34. Nitric Acid as an Oxidizing Agent.**—The conditions for the reduction of nitric acid to  $\text{NO}$ ,  $\text{NO}_2^-$ , or  $\text{NO}_2$  have



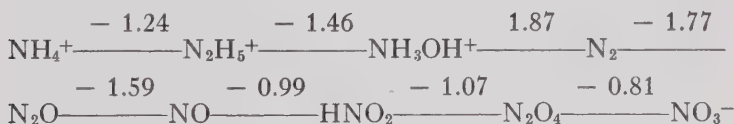
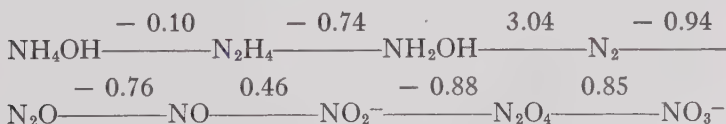
been discussed (Par. 29). The further reduction to  $\text{NH}_3$  with  $\text{SO}_2$  has also been treated (Par. 30) and this step may be carried out with Zn and other powerful reducing agents. The values for a number of the oxidation-reduction potentials at molal concentration are given below, but it must be pointed out that in the majority of the reactions the rates are slow, and that the speed becomes a factor of equal importance with the energy in determining what reactions will occur.

TABLE X

OXIDATION-REDUCTION POTENTIALS OF  $\text{HNO}_3$  AND  $\text{NO}_3^-$ 

<i>Acidic solution</i>	VOLTS <sub>25°</sub>
$\text{H}_2\text{O} + \text{NO}_2 = \text{NO}_3^- + 2\text{H}^+ + e^-$ .....	- 0.81
$\text{H}_2\text{O} + \text{HNO}_2 = \text{NO}_3^- + 3\text{H}^+ + 2e^-$ .....	- 0.94
$2\text{H}_2\text{O} + \text{NO} = \text{NO}_3^- + 4\text{H}^+ + 3e^-$ .....	- 0.96
$5\text{H}_2\text{O} + \text{N}_2\text{O} = 2\text{NO}_3^- + 10\text{H}^+ + 8e^-$ .....	- 1.11
$3\text{H}_2\text{O} + \frac{1}{2}\text{N}_2 = \text{NO}_3^- + 6\text{H}^+ + 5e^-$ .....	- 1.24
$2\text{H}_2\text{O} + \text{NH}_3\text{OH}^+ = \text{NO}_3^- + 8\text{H}^+ + 6e^-$ .....	- 0.73
$6\text{H}_2\text{O} + \text{N}_2\text{H}_5^+ = 2\text{NO}_3^- + 17\text{H}^+ + 14e^-$ .....	- 0.84
$3\text{H}_2\text{O} + \text{NH}_4^+ = \text{NO}_3^- + 10\text{H}^+ + 8e^-$ .....	- 0.87

The potentials for the oxidation of ammonia by steps in both acidic and basic solutions are shown in the following scheme:

*Acidic solution:**Basic solution:*

Although the reduction to free nitrogen appears to give the greatest potential, this reaction is seldom realized, and then usually through the formation, first, of a compound of

nitrogen of negative oxidation number which reacts with nitrogen compounds of the same positive oxidation number, e.g.  $\text{NH}_4^+ + \text{NO}_2^- = \text{N}_2 + \text{H}_2\text{O}$  and  $\text{NH}_2\text{OH} + \text{NOH} = \text{N}_2 + 2\text{H}_2\text{O}$  (Par. 26). The values in the table show that nitrate in alkaline solution is not a powerful oxidizing agent. The values in the table apply to molal concentrations and cannot be used to predict the action of concentrated nitric acid, which is a far more powerful oxidizing agent, especially when heated. Nitric acid is reduced by sulfurous acid or acid sulfites through the formation of nitrosylsulfuric acid,  $\text{HONO}_2 + \text{H}_2\text{SO}_3 = \text{HSO}_3 \cdot \text{NO}_2 + \text{H}_2\text{O}$ , and its subsequent hydrolysis in dilute acid:  $\text{HSO}_3 \cdot \text{NO}_2 + \text{H}_2\text{O} = \text{HNO}_2 + \text{H}_2\text{SO}_4$ . (See Par. 31 for continuation of reduction process.)

**35.** Nitric acid reacts with chloride ion according to the equation:  $4\text{H}^+ + \text{NO}_3^- + 3\text{Cl}^- = \text{NOCl} + \text{Cl}_2 + 2\text{H}_2\text{O}$ . The compound,  $\text{NOCl}$ , is **nitrosyl chloride**, a liquid boiling at  $-5.6^\circ$ , and upon heating, it very readily decomposes into nitric oxide and chlorine. The mixture of nitric and hydrochloric acids, known as **aqua regia**, is capable of dissolving gold and platinum, which will not dissolve in nitric acid alone. This, however, is not due to an increase in the oxidizing potential of the nitric acid in the presence of the chloride, but rather to an increase in the reduction potential of these metals in the presence of the chloride (cf. VII—31).

**36.** Nitric acid reacts with organic hydroxides to form nitrates, for example with glycerine to form "nitroglycerine,"  $\text{C}_3\text{H}_5(\text{OH})_3 + 3\text{HNO}_3 = \text{C}_3\text{H}_5(\text{NO}_3)_3 + 3\text{H}_2\text{O}$ , and with hydrocarbons, such as benzene, to form nitro compounds such as nitrobenzene:  $\text{C}_6\text{H}_6 + \text{HNO}_3 = \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$ . In both of these reactions, water is produced, so that the reaction is favored by the presence of concentrated sulfuric acid to lower the activity of this product. Large quantities of the mixed concentrated acids are manufactured for this purpose. At present, the major portion of the nitric acid manufactured is consumed in some form of

organic nitrate or nitro-compound, the more important being the explosives, plastics, varnishes, and dyes (cf. XIII—29).

**37. Nitrates.**—The nitrates of the metals are, in general, readily soluble in water. The nitrate group shows but slight tendencies to form coordination compounds. The alkali nitrates decompose upon heating to form nitrites:  $2\text{NaNO}_3 = 2\text{NaNO}_2 + \text{O}_2$ . The nitrates of the more noble metals form the dioxide, e.g.  $2\text{Cu}(\text{NO}_3)_2 = 2\text{CuO} + 4\text{NO}_2 + \text{O}_2$ . Ammonium nitrate decomposes into nitrous oxide and water:  $\text{NH}_4\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$ .

X-ray data on the crystalline nitrates show that the three oxygen atoms are arranged symmetrically about the nitrogen atom in the same plane.

The properties of many nitrates have been discussed under the various positive constituents, the more important being the salts of sodium, potassium, ammonia, and calcium. Formerly the largest use of a nitrate was in the manufacture of **gunpowder**, consisting of potassium nitrate, 75 per cent; charcoal, 15 per cent; and sulfur 10 per cent. This mixture is moistened, ground, and the dried product granulated. When ignited, the powder burns and liberates a large volume of gases consisting mainly of nitrogen, carbon dioxide, carbon monoxide, and some sulfur dioxide. This type of powder is not smokeless, since solid particles of potassium sulfide and oxide are dispersed in the gas phase.

**38. Peroxynitrogen Compounds.**—Nitric oxide appears to unite with oxygen at low temperature ( $-180^\circ$ ) to form the peroxide,  $\text{NO}_3$ , which decomposes upon heating. The silver salt of the peroxynitric acid,  $\text{HNO}_5$ , is said to be formed by the electrolysis of a concentrated solution of silver nitrate, but neither the free acid nor other salts have been prepared. The highly unstable acid,  $\text{HNO}_4$ , is formed by the action of hydrogen peroxide upon nitrogen pentoxide:  $\text{H}_2\text{O}_2 + \text{N}_2\text{O}_5 = \text{HNO}_4 + \text{HNO}_3$ .

**39. Analytical.**—The ferrous sulfate test for nitrates depends upon the reduction of nitrates by ferrous ion in concentrated hydrogen ion solution and the formation of the brown complex ion,  $\text{Fe}(\text{NO})^{++}$ . The test may be carried out by the addition of about 5 cc. of ferrous sulfate solution to a few cc. of unknown solution. Holding the tube in an inclined position, 36*N*  $\text{H}_2\text{SO}_4$  is carefully poured down the side of the tube so that the two liquids do not mix. A brown ring at the junction of the two liquids indicates nitrate. The test is not satisfactory in the presence of chlorate, iodine, bromine, nitrite, ferrocyanide, or ferricyanide. The diphenylamine test for nitrates consists of the addition of a solution of  $(\text{C}_6\text{H}_5)_2\text{NH}$  in sulfuric acid to 2 or 3 cc. of unknown solution on a watch glass. Upon gentle heating, a blue color is produced if a nitrate is present.

The quantitative determination of nitrate is usually carried out either by reduction to ammonia and the determination as such, or the reduction to nitric oxide, and its estimation as a gas (nitrometer method). In the former process, aluminum or Devarda's alloy (Al 45, Cu 50, Zn 5) in alkaline solution is used as the reducing agent. The ammonia is distilled into excess standardized sulfuric acid, and the excess of acid titrated with sodium hydroxide. The nitrometer process depends upon the reaction:  $2\text{NO}_3^- + 8\text{H}^+ + 3\text{SO}_4^{--} + 6\text{Hg} = 3\text{Hg}_2\text{SO}_4 + 4\text{H}_2\text{O} + 2\text{NO}$ . The nitric oxide is collected in a gas burette or nitrometer and the quantity of nitrate calculated from the volume of gas. The base diphenylendoanilohydrotriazole,  $\text{C}_{20}\text{H}_{16}\text{N}_4$ , called **nitron**, forms a slightly soluble nitrate,  $\text{C}_{20}\text{H}_{16}\text{N}_4 \cdot \text{HNO}_3$ , and this reagent can be used for the quantitative separation and estimation of nitric acid.

## PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

**40.** The elements of this group form an especially interesting series in that they involve a complete transition from

non-metallic to metallic character in both physical and chemical properties. It is, however, noteworthy that this transition is by no means uniform, but that there is rather an alternation in properties. Thus, nitrogen, arsenic, and bismuth form no pentachlorides, while phosphorus and antimony do. Figure 1 illustrates this alternation for the heats of formation of the trioxides and trichlorides when plotted against atomic numbers. This alternation extends to neighboring groups, as illustrated first by figures for the heats of formation of the dioxides of Group VI and second, in Group VII, by the stability of oxides of chlorine and iodine, but not of fluorine or bromine. Various other evidences of alternation may be discovered, such as the enhanced tendency towards hydration of the oxides of phosphorus and antimony as compared with those of their immediate neighbors.

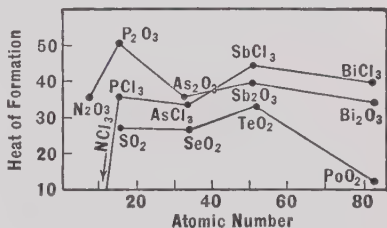


FIG. 1. Heats of formation in kcal. per equivalent against atomic numbers.

**41. Occurrence.**—Phosphorus is the only member of the group which is never found free in nature. It occurs principally as calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , and as apatite,  $\text{Ca}_5\text{F}(\text{PO}_4)_3$  and  $\text{Ca}_5\text{Cl}(\text{PO}_4)_3$ . The first of these is found in large deposits of phosphate rock in Florida, Tennessee, Montana, and neighboring states, and in northern Africa. It is the principal mineral constituent of bones and teeth, and bone ash is largely calcium phosphate. Apatite occurs in many rocks, and important deposits are located in Canada. Many plant and animal tissues contain phosphoproteins, complex compounds of protein with phosphoric acid derivatives, such as casein in milk, and vitellin in eggs. The average human body daily excretes phosphorus compounds containing about 2 g. of the element.

Arsenic and antimony are occasionally found free, and

bismuth is generally so found. Their most important minerals are the sulfides: arsenical pyrite,  $\text{FeAsS}$ ; orpiment,  $\text{As}_2\text{S}_3$ ; realgar,  $\text{As}_2\text{S}_2$ ; stibnite,  $\text{Sb}_2\text{S}_3$ ; bismuthinite,  $\text{Bi}_2\text{S}_3$ . Oxides also occur such as claudetite,  $\text{As}_2\text{O}_3$ ; senarmontite,  $\text{Sb}_2\text{O}_3$ ; and bismite,  $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , and less frequently selenides and tellurides. Arsenides, such as  $\text{FeAs}_2$ ,  $\text{CoAs}_2$ , and  $\text{NiAs}$  are not infrequent, and arsenic is a common impurity in sulfuric acid made from pyrites, in pig iron, and in commercial zinc. The most extensive deposits of antimony are located in China. The average percentage of the metals in the igneous rocks is given as: arsenic,  $10^{-6}$ , antimony  $10^{-7}$ , and bismuth  $10^{-8}$ .

**42. Properties of the Elements.**—The more important physical constants are summarized in Table XI. Like the corresponding elements of Group VI, phosphorus, arsenic, and antimony exist in a number of crystalline modifications. **Phosphorus** has the two familiar forms known as “white” and “red.” The white modification is formed by rapidly cooling phosphorus vapor. It is a wax-like substance, of low melting point, very low heat of fusion (157 cal. per g. atom), high volatility even at room temperature

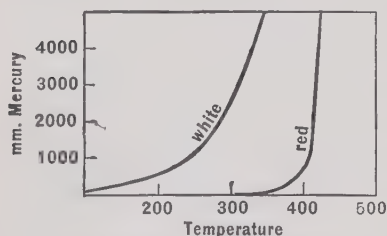


FIG. 2. Vapor pressure of phosphorus.

(Fig. 2) and is readily soluble in carbon disulfide (90 g. per 100 g. sol. at  $10^\circ$ ). It ignites spontaneously in air and is, therefore, usually kept and worked under water in which it is only very slightly soluble (1 in 300,000). It is extremely poisonous, about 0.1 g. being a fatal dose, and the continued consumption of small amounts leads to chronic poisoning, one of the symptoms of which is necrosis of the jaw. The white is a metastable form and upon heating or exposure to sunlight turns yellow and then red. The transition is catalyzed by iodine: a trace of the latter causes a



very rapid reaction at  $200^{\circ}$ . The heat of the transition is 3,700 cal.

The red modification does not have definite density or melting point and appears to be a transition form or mixture of the white and the real stable modification, **violet phosphorus**. The latter is difficult to prepare pure, but may be obtained by crystallization from a solution in molten lead. The properties of red phosphorus are essentially those of the violet. It is much less volatile than the white and is not appreciably soluble in carbon disulfide or other solvents. Red phosphorus sublimes without melting, unless heated under pressure, and from the shape of the vapor pressure curves there does not appear to be a transition point between the two modifications. Red phosphorus is not especially reactive, only slightly poisonous, and does not ignite below  $240^{\circ}$ . White phosphorus has a molecular weight corresponding to  $P_4$  in its solutions and in the vapor state, but the red or violet is not sufficiently soluble to enable its molecular weight to be determined. Above  $1,500^{\circ}$ , the vapor is somewhat dissociated into  $P_2$ . A third solid modification, **black phosphorus**, is formed when a pressure of 4,000 atmospheres is applied to the element at  $200^{\circ}$ .

Arsenic exists in a reactive metastable crystalline modification, the so-called "yellow" arsenic, and a grey semi-metallic form. **Yellow arsenic** is formed by passing the vapor into cold carbon disulfide. The rate of transition into the grey form is rapid even at low temperature and instantaneous at room temperature in the sunlight. Yellow arsenic volatilizes readily, is extremely poisonous and phosphoresces in air at room temperature. Its molecular weight in solution corresponds to  $As_4$ . The **metallic form** is steel grey in color with a bright luster, very brittle, and is a good conductor of heat but a rather poor electrical conductor. It sublimes without melting unless heated under pressure.

Antimony occurs in modifications similar to those of

arsenic. **Yellow antimony** is transformed so rapidly into the stable form that it can be kept only at low temperature. Antimony also forms a metastable metallic modification known as **explosive antimony** from the character of its transition into the stable form when struck or scratched. The reaction evolves 20 cal. of heat per gram. Yellow antimony is formed by the action of oxygen upon liquid stibine,  $\text{SbH}_3$ , at  $-90^\circ$ , and the explosive form by the electrolysis of a concentrated solution of antimony trichloride. The explosive form always contains some trichloride, and is probably a solid solution of the chloride in yellow antimony. The stable modification is a silvery white, metallic appearing substance. It is extremely brittle and much less volatile than arsenic.

**Bismuth** is known only in the one crystalline metallic form. It is grey white with a slight red tinge, hard and brittle, a very poor conductor of heat, and, although its melting point is low, the boiling point is high.

**43. Preparation of the Elements.**—Phosphorus is generally prepared from calcium phosphate through the reaction,  $\text{Ca}_3(\text{PO}_4)_2 + 3\text{SiO}_2 + 5\text{C} = 3\text{CaSiO}_3 + 5\text{CO} + \text{P}_2$ , which is carried out at high temperatures, usually in an electric arc furnace. Phosphorus vapor leaves the furnace along with the carbon monoxide and is condensed under water, while the calcium silicate is drawn off as liquid slag. The element was first prepared by Brandt in 1669, by the destructive distillation of the solid residue from the evaporation of urine.

Arsenic, antimony, and bismuth may be obtained by the reduction of the oxides with carbon, e.g.,  $\text{As}_2\text{O}_3 + 3\text{C} = 2\text{As} + 3\text{CO}$ . In case the ore is a sulfide, it may first be roasted to the oxide:  $2\text{As}_2\text{S}_3 + 9\text{O}_2 = 2\text{As}_2\text{O}_3 + 6\text{SO}_2$ ; or iron may be used as the reducing agent:  $\text{Sb}_2\text{S}_3 + 3\text{Fe} = 2\text{Sb} + 3\text{FeS}$ . Native bismuth is easily extracted by taking advantage of its low melting point, and simply heating the ore and running off the metal. Most of the bismuth is obtained as a

by-product of copper, lead, gold, and silver ores, generally from the flue dust of the smelters.

TABLE XI

ATOM AND PHYSICAL PROPERTIES OF PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

	P	As	Sb	Bi
Atomic weight.....	31.02	74.91	121.76	209.00
Atomic number.....	15	33	51	83
Isotopes.....	31	75	121, 123	209 (210) (214)
Electrons in various quantum states,				
1st.....	2	2	2	2
2d.....	8	8	8	8
3d.....	5	18	18	18
4th.....		5	18	32
5th.....			5	18
6th.....				5
Ionization of gaseous atom, volts.....	10.9	10.5	9?	8?
Size of $M^{+5}$ ion, cm. $\times 10^8$ .....	0.34	0.47	0.62	0.74
Molecular formula of gas at boiling point	$P_4$	$As_4 - As_2$	$Sb_2 - Sb$	$Bi_2 - Bi$
Melting point.....	W 44.1° V 590 (43 atm.)	814° (36 atm.)	630.5°	271°
Boiling point.....	280°	610° (sub.)	1440°	1420°
Density.....	W 1.82 V 2.34	M 5.7 Y 3.9	M 6.58 Y 5.3	9.8
Electrical resistivity, ohm-cm.....	W $10^{11}$ , $10^9$	$35 \times 10^{-6}$ , $0^\circ$	$39 \times 10^{-6}$ , $20^\circ$	$115 \times 10^{-6}$ , $20^\circ$
$G + 3H_2O = H_3GO_3 + 3H^+ + 3e^-$ volts	0.49	- 0.25	$Sb = SbO^+ - 0.21$	$Bi = BiO^+ - 0.32$

**44. Commercial Applications of the Elements.**—The electric furnace production of phosphorus has increased rapidly since 1937. The element is shipped in tank cars and most of it is later burned to  $P_2O_5$  and made into various phosphates. A large amount of the phosphorus is consumed in the preparation of the sulfide,  $P_4S_3$  (Par. 62), for use in **matches**. Formerly matches were made by dipping wood splints into a paste containing white phosphorus, lead dioxide, powdered glass, and glue. Due to its poisonous nature, the use of white phosphorus is now prohibited in most countries and in its place the trisulfide is substituted. When struck, the friction raises the temperature to the point where the phosphorus sulfide is rapidly oxidized by the

lead dioxide and the match bursts into flame. In the so-called "bird's eye" match, the phosphorus sulfide is present only in the small tip. The safety matches now used so extensively contain no phosphorus in the match head, but the box is coated with a mixture of red phosphorus, glue, and abrasive. The match contains a mixture of good oxidizing agents, such as potassium chlorate or chromate or lead dioxide, and reducing agents, as antimony sulfide. It may be ignited by striking on some surface of low heat conductivity, such as glass, and more readily on the surface of the box, since a trace of the red phosphorus is ignited by the friction and the heat kindles the match head.

Phosphorus is used in tracer bullets, and burning phosphorus is employed for the preparation of smoke screens. Ground with flour and grease, white phosphorus is used as a poison for rodents.

Very little free arsenic is consumed. The annual consumption in the United States is around 100 tons. A small amount of element (0.5 per cent) is usually added to lead in making shot to harden it and also to increase the surface tension. The latter aids in obtaining perfect spheres when the shot is made by allowing molten drops to fall from a height. The use of arsenic as a metal-tempering material is increasing. Arsenical copper alloys are now employed in products which require soldering, as their annealing temperature is high and the substance does not suffer loss of strength during heating. The trioxide is an important commercial compound.

Antimony is a cheap metal which can be used in certain instances as a substitute for more expensive metals. Most of the world's supply comes from China. The annual consumption in the United States is about 20,000 tons. Its principal use is in the manufacture of alloys, especially those of lead and tin, the most important being type metal, white metal, hard metal, britannia, babbitt, and antifric-tion metal (see Alloys of Lead and Tin). The presence of

antimony adds to the hardness of the metal and also contributes the property of expanding upon solidification, which makes these alloys very useful in the preparation of sharp castings. About half of the American consumption goes into a lead alloy for battery plates.

Bismuth alloys also expand upon cooling and make good castings. A number of bismuth alloys can be prepared which melt below the boiling point of water, e.g.

	M.P.	Bi	Pb	Sn	Cd
Lipowitz metal . . . . .	60°	50	27	13	10
Woods metal . . . . .	71°	50	25	12.5	12.5
Rose metal . . . . .	94°	50	27.1	22.9	—

Alloys of this type are used in automatic fire extinguishers which depend upon plugs of the alloy melting and releasing water sprinklers, closing fire-doors, etc. Such alloys are also employed in safety plugs in steam boilers to guard against over-heating. An alloy of 55.5 per cent Bi and 44.5 per cent Pb is utilized as a master pattern metal in the foundry industry. An aluminum alloy (Al, 93.5; Cu, 5.5; Pb, 0.5; Bi, 0.5) is free cutting and is used as the material for aluminum screws.

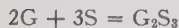
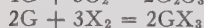
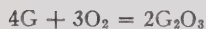
**45. Reactions of the Elements.**—The reactions of phosphorus are markedly different for the two modifications. Yellow phosphorus in moist air at ordinary temperature emits a pale greenish light and gives off white fumes of the sesquioxide, and the reaction is accompanied by the formation of ozone. The light is not true temperature radiation but results from the conversion of some of the reaction energy directly into light (**chemiluminescence**). The glow appears to be connected with the formation of trioxide and does not occur if the partial pressure of the oxygen is considerably increased, although oxidation to the pentoxide then takes place. Yellow phosphorus ignites at about 45°, the red at about 260°. The yellow modification likewise

ignites spontaneously in chlorine, but the red must be heated to start the reaction. Yellow phosphorus is also soluble in hot alkalis liberating phosphine while the red is not although the energy of the reaction is favorable. Phosphorus reacts with sulfur forming sulfides and with the halogens (Par. 61). Moderately strong oxidizing agents oxidize phosphorus to phosphoric acid;  $P + 4H_2O = H_3PO_4 + 5H^+ + 5e^-$ ; + 0.3 volt. The potential value indicates that even hydrogen ion should be capable of oxidizing the element but the oxidation appears to be slow with all weak oxidizing agents.

Arsenic, antimony, and bismuth form surface films of oxide in moist air, and burn to the trioxide when heated (Sb also forms some  $Sb_2O_4$ ). Like phosphorus, they unite directly when heated with sulfur (Par. 62), the halogens (Par. 61), and various metals (Par. 63). The oxidation of the elements to the + 5 state becomes increasingly difficult with increasing atomic weight. Concentrated nitric acid, acting upon the elements, forms  $H_3AsO_4$ ,  $Sb_2O_5$ , and  $Bi(NO_3)_3$ . The reactions are summarized in Table XII.

TABLE XII

REACTIONS OF PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH  
(G = any element of the group)



See also  $P_2O_5$  and  $Sb_2O_4$

X = halide. See also Par. 61 for  $GX_5$ , etc.

See Par. 62 for other sulfides

Formation of metal phosphides, arsenides, antimonides, and bismuthides

**46. Hydrogen Compounds.**—Gaseous hydrogen compounds the analogues of ammonia, are formed by all members of the group: **phosphine**,  $PH_3$ ; **arsine**,  $AsH_3$ ; **stibine**,  $SbH_3$ ; **bismuthine**,  $BiH_3$ . They are frequently referred to as hydrides, but since the hydrogen is undoubtedly more positive, the name does not appear to be appropriate.



TABLE XIII  
PHYSICAL PROPERTIES OF HYDROGEN COMPOUNDS

	NH <sub>3</sub>	PH <sub>3</sub>	AsH <sub>3</sub>	SbH <sub>3</sub>	BiH <sub>3</sub>
Melting point, °C. ....	- 75	- 132.5	- 119	- 88	?
Boiling point, °C. ....	- 33.5	- 86.2	- 55	- 18	?
Heat of formation, kcal. ....	10.2	1.9	- 36.7	- 34?	?
XH <sub>3</sub> = X( $\frac{1}{2}$ N <sub>2</sub> ) + 3H <sup>+</sup> + 3e <sup>-</sup>					
volts. ....	- 0.27	0.03	0.54	0.51?	(0.8)

**47.** Unlike ammonia, the other members of the group cannot be prepared by the direct union of the element and hydrogen. Phosphine decomposes readily upon heating; stibine decomposes explosively, and the bismuth compound is so unstable that a quantity of the gas is 80 per cent decomposed in 50 minutes at room temperature. The decomposition of arsine and stibine is further considered under the Marsh test (Par. **64**).

A general method of preparation is the hydrolysis of a binary metal compound similar to the hydrolysis of magnesium nitride to form ammonia:  $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} = 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$ ;  $\text{Na}_3\text{As} + 3\text{H}_2\text{O} = 3\text{NaOH} + \text{AsH}_3$ ;  $\text{Zn}_3\text{Sb}_2 + 6\text{H}_2\text{O} = 3\text{Zn}(\text{OH})_2 + 2\text{SbH}_3$ ;  $\text{Mg}_3\text{Bi}_2 + 6\text{H}_2\text{O} = 3\text{Mg}(\text{OH})_2 + 2\text{BiH}_3$ .

Phosphine may also be prepared by boiling white phosphorus with a solution of an alkali:  $4\text{P} + 3\text{OH}^- + 3\text{H}_2\text{O} = 3\text{H}_2\text{PO}_2^- + \text{PH}_3$ . There are usually present in the gas traces of the compounds  $\text{P}_2\text{H}_4$  and  $\text{P}_4\text{H}_2$ .

Arsine may be formed by cathodic reduction, or by the reduction of arsenic compounds in acid solution by zinc or magnesium:  $\text{H}_3\text{AsO}_3 + 3\text{Zn} + 6\text{H}^+ = \text{AsH}_3 + 3\text{Zn}^{++} + 3\text{H}_2\text{O}$ . This reduction gives, of course, a mixture of the gas and hydrogen. The same method is also applicable to the preparation of stibine, but the more powerful reducing agent, magnesium, must be used for bismuthine.

These compounds are all extremely poisonous and it is dangerous to inhale even small amounts. Because of the

presence of arsenic in many acids and metals, arsine is a common impurity in hydrogen prepared through their interaction, and such hydrogen should, therefore, not be inhaled unless it has been passed through permanganate solution.

Phosphine ignites spontaneously in air. The gas burns to phosphoric acid:  $\text{PH}_3 + 2\text{O}_2 = \text{H}_3\text{PO}_4$ . If bubbled through water into air, the bubbles ignite at the surface and form beautiful smoke rings. Arsine and stibine readily burn in air, forming the trioxides. If, however, a piece of cold porcelain is placed in the flame, it is coated with the free element. The liquid compound,  $\text{P}_2\text{H}_4$ , decomposes in the light into phosphine and a hydrogen phosphide,  $\text{P}_4\text{H}_2$ , or possibly  $\text{P}_{12}\text{H}_6$ , which is a solid:  $5\text{P}_2\text{H}_4 = 6\text{PH}_3 + \text{P}_4\text{H}_2$ .

**48.** Unlike ammonia, these compounds are only slightly soluble in water ( $\text{PH}_3$ , 11 vol. in 100 vol. water at  $15^\circ$ ), and the solutions are not alkaline. The basic nature of the compounds decreases with the increasing size of the elements. Indeed, phosphine is the only one which resembles ammonia in the formation of salts, the **phosphonium compounds**, and these are far less stable than the ammonium compounds.

Phosphonium iodide,  $\text{PH}_4\text{I}$ , is formed by the reaction:  $\text{PH}_3 + \text{HI} = \text{PH}_4\text{I}$ . It crystallizes in beautiful, large, highly refracting, square, prisms which sublime at  $62^\circ$ . It is a powerful reducing agent, and is decomposed by water with the liberation of phosphine. Phosphonium bromide resembles the iodide, but the chloride can only be formed at room temperature under pressure (at  $14^\circ$  the dissociation pressure,  $\text{PH}_4\text{Cl} = \text{PH}_3 + \text{HCl}$ , is about 20 atmospheres).

Phosphine reacts with solutions of certain metallic ions, e.g.  $\text{Cu}^{++}$ , with the formation of slightly soluble metal phosphides, which usually are of uncertain composition. Arsine passed into a solution of silver nitrate gives metallic silver and arsenious acid:  $\text{AsH}_3 + 6\text{Ag}^+ + 3\text{H}_2\text{O} = 6\text{Ag} + \text{H}_3\text{AsO}_3 + 6\text{H}^+$ . Under the same conditions, stibine

gives silver antimonide:  $\text{SbH}_3 + 3\text{Ag}^+ = 3\text{H}^+ + \text{Ag}_3\text{Sb}$ . Arsenic forms no compounds analogous to hydrazine but organic derivatives are known, such as  $\text{As}_2(\text{CH}_3)_4$ , **cacodyl**.

### OXIDES AND ACIDS

49. The oxides and acids are summarized in Table XIV.

TABLE XIV

ACIDS AND OXIDES OF PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

OXIDATION STATE		P	As	Sb	Bi
	<i>Oxides</i>				
2	Monoxide	.....	.....	.....	BiO
3	"Trioxide" (or $\text{X}_4\text{O}_6$ )	$\text{P}_2\text{O}_3$	$\text{As}_2\text{O}_3$	$\text{Sb}_2\text{O}_3$	$\text{Bi}_2\text{O}_3$
4	Tetroxide	$\text{P}_2\text{O}_4$	$\text{As}_2\text{O}_4(?)$	$\text{Sb}_2\text{O}_4$	$\text{Bi}_2\text{O}_4$
5	Pentoxide	$\text{P}_2\text{O}_5$	$\text{As}_2\text{O}_5$	$\text{Sb}_2\text{O}_5$	$\text{Bi}_2\text{O}_5$
	<i>Acids</i>				
1	Hypo-us	$\text{H}_3\text{PO}_2$	.....	.....	.....
3	-ous { meta	.....	$\text{HAsO}_2$	$\text{HSbO}_2$	.....
	ortho	$\text{H}_3\text{PO}_3$	$\text{H}_3\text{AsO}_3$	$\text{H}_3\text{SbO}_3$	$\text{Bi}(\text{OH})_3$
	pyro	$\text{H}_4\text{P}_2\text{O}_5$	.....	.....	.....
4	Hypo-ic	$\text{H}_4\text{P}_2\text{O}_6$	.....	.....	.....
	meta	$\text{HPO}_3$	$\text{HAsO}_3$	$(\text{HSbO}_3)$	$\text{HBiO}_3$
5	-ic { ortho	$\text{H}_3\text{PO}_4$	$\text{H}_3\text{AsO}_4$	$\text{HSb}(\text{OH})_6$	.....
	pyro	$\text{H}_4\text{P}_2\text{O}_7$	$\text{H}_4\text{As}_2\text{O}_7$	.....	.....
	tetra	$\text{H}_6\text{P}_4\text{O}_{13}$	.....	.....	.....

Peroxyacids of phosphorus,  $\text{H}_4\text{P}_2\text{O}_8$  and  $\text{H}_3\text{PO}_5$ , also exist. The pentoxides, with the exception of that of phosphorus, readily evolve oxygen upon heating, forming the sesquioxides. These oxides are formed also upon burning the elements in air. Measurements of gas density show that the sesquioxides, generally called the trioxides, are associated into double molecules,  $\text{X}_4\text{O}_6$ . Phosphorus pentoxide has an enormous affinity for water, even removing it from concentrated sulfuric acid. The oxides of arsenic react slowly with water, while the oxides of antimony and bismuth show almost no such reaction. With increasing size of the atoms, the oxides become less acidic.

50. **Oxides and Acids of Phosphorus.**—The sesquioxide,  $\text{P}_2\text{O}_3(\text{P}_4\text{O}_6)$ , is produced by the combustion of phosphorus

in a limited supply of air. It dissolves slowly in cold water, to form phosphorous acid, and violently in hot water, to form phosphoric acid and phosphine:  $2\text{P}_2\text{O}_3 + 6\text{H}_2\text{O} = \text{PH}_3 + 3\text{H}_3\text{PO}_4$ . When heated in a sealed tube, it decomposes into the tetroxide and phosphorus:  $4\text{P}_2\text{O}_3 = 3\text{P}_2\text{O}_4 + 2\text{P}$ . The trioxide is readily separated from the pentoxide by the greater volatility of the former. The heat of formation of  $\text{P}_2\text{O}_5$  from its elements is about 370 kcal., and the heat of solution in water to form orthophosphoric acid,  $\text{H}_3\text{PO}_4$ , is about 35 kcal. The pentoxide appears to exist in a number of forms, one of which sublimes at about  $350^\circ$ . The

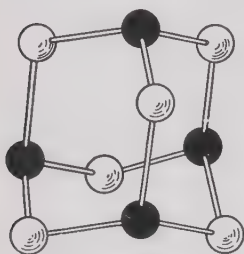
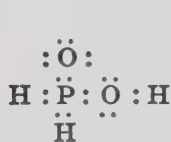


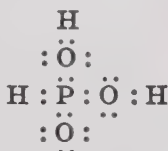
FIG. 3. Structure of  $\text{P}_4\text{O}_6$  and  $\text{As}_4\text{O}_6$ .

vapor density of the higher oxide corresponds to the formula  $\text{P}_4\text{O}_{10}$  even at  $1500^\circ$ . Frequent mention has been made of the oxide as an extremely efficient drying agent.

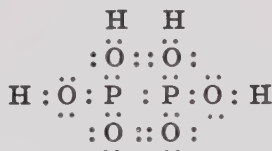
Electronic formulas for the more important phosphorus acids are given below:



Hypophosphorous acid



Phosphorous acid



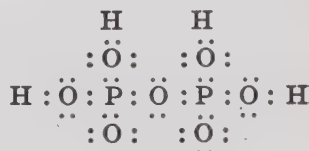
Hypophosphoric acid



Orthophosphoric acid



Metaphosphoric acid



Pyrophosphoric acid

The formulas for hypophosphorous acid and phosphorous acid have been written with two and one hydrogen atoms,

respectively, attached to the phosphorus. This is in agreement with the fact that the former acts only as a monobasic acid and the latter generally as a dibasic acid, and also that these acids are fairly strong (even stronger than phosphoric acid—see Table XV), whereas the general rule that the higher the positive oxidation state, the stronger the acid, would predict that they would be very weak acids, since phosphoric acid is, itself, only moderately strong. In other words, it seems probable that the hydrogen attached to phosphorus serves to attract electrons, and thus increase the effective charge on the central atom.

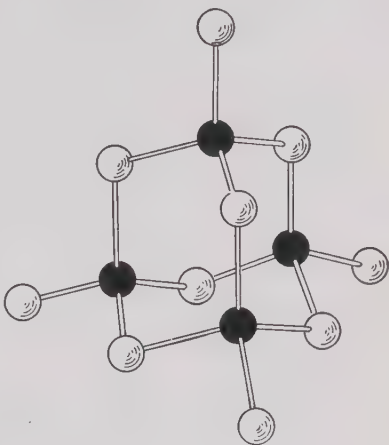
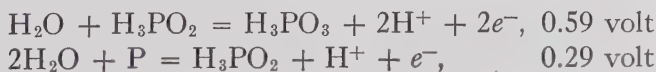
FIG. 4. Structure of  $P_4O_{10}$ .

TABLE XV  
CONDUCTIVITY OF PHOSPHORUS ACIDS

	$H_3PO_2$	$H_3PO_3$	$H_3PO_4$
Equivalent Conductivity . . . . .	281	257	156

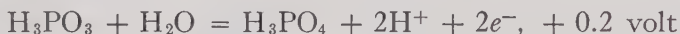
**51.** Salts of **hypophosphorous acid**,  $H(H_2PO_2)$ , are obtained by the action of phosphorus on an alkaline solution (Par. 47). The free acid may be prepared by treating the barium salt with sulfuric acid. The acid is a strong reducing agent and a poor oxidizing agent:



When heated, it decomposes into phosphine and phosphoric acids. The sodium salt,  $NaH_2PO_2$ , is used in medicine

under the belief that phosphorus can thus be supplied to the body tissues. As mentioned above, the acid is monobasic and highly ionized in solution.

**52. Phosphorous acid**,  $\text{H}_2(\text{HPO}_3)$ , is formed by the action of the trioxide upon cold water, or by the hydrolysis of the trichloride:  $\text{PCl}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{HCl}$ . The further addition of the chloride gives the pyro-acid,  $\text{H}_4\text{P}_2\text{O}_5$ . The acid decomposes upon heating to give pure phosphine and phosphoric acid. The acid is oxidized to phosphoric acid:



but a moderately strong oxidizing agent is required as the first step is probably



**53. Hypophosphoric acid**,  $\text{H}_4\text{P}_2\text{O}_6$ , may be formed, mixed with phosphorous acid, by the slow oxidation of phosphorus in a limited supply of moist air. It is tetrabasic, and its salts are relatively unimportant.

**54. The Phosphoric Acids and Phosphates.**—The product of the addition of phosphorus pentoxide to an excess of water is a solution of the orthophosphoric acid,  $\text{H}_3\text{PO}_4$ . This acid, or its hydrate,  $2\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ , may be crystallized from the solution by evaporating under reduced pressure. The pure acid melts at  $42.3^\circ$  and the hydrate at  $29.4^\circ$ . The acid is tribasic, and thus forms three series of salts. The ionization constants for the acid are, respectively,  $K_1 = 7.5 \times 10^{-3}$ ,  $K_2 = 6.2 \times 10^{-8}$ ,  $K_3 = 10^{-12}$ . The values for the molal concentration of  $\text{H}^+$  in molal solutions of the following are:  $\text{H}_3\text{PO}_4$ , 0.1;  $\text{NaH}_2\text{PO}_3$ ,  $2 \times 10^{-4}$ ;  $\text{Na}_2\text{HPO}_4$ ,  $10^{-8}$ ;  $\text{Na}_3\text{PO}_4$ ,  $10^{-13}$ .

Phosphoric acid is but a very weak oxidizing agent (Par. 52). In this respect, it differs greatly from the other +5 acids of the group.

Impure commercial acid is made by heating pulverized phosphate rock with sulfuric acid:  $\text{Ca}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4$



$= 2\text{H}_3\text{PO}_4 + 3\text{CaSO}_4$ . The greater portion of the calcium sulfate formed in the reaction is precipitated and separated by filtration. The acid is also manufactured by a method similar to the preparation of the free element by heating phosphate rock with carbon and sand, but differing in that air is introduced to oxidize the phosphorus vapor to the pentoxide, which is absorbed in water.

The most important salts of orthophosphoric acid are the calcium compounds. The occurrence of enormous deposits of the slightly soluble **tricalcium phosphate** has been mentioned. Soluble phosphate constitutes an important constituent of fertile soils and large quantities of phosphate rock (U. S. production about 4,000,000 tons yearly) are mined and converted

into the soluble salt,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , for use as fertilizer:  $\text{Ca}_3(\text{PO}_4)_2 + 2\text{H}_2\text{SO}_4 + 4\text{H}_2\text{O} = \text{Ca}(\text{H}_2\text{PO}_4)_2 + 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . The mixture of acid phosphate and gypsum is sold under the name of "**superphosphate of lime.**" **Triple superphosphate** is made by the action of phosphoric acid on phosphate rock,  $\text{Ca}_3(\text{PO}_4)_2 + 4\text{H}_3\text{PO}_4 = 3\text{Ca}(\text{H}_2\text{PO}_4)_2$ . It seems likely that **ammonium phosphate** will to a certain extent replace the superphosphate as a fertilizer (Par. 17).

Most of the normal orthophosphates are but slightly soluble. The compounds, **ammonium magnesium phosphate**,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , and **ammonium phosphomolybdate**,  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ , are mentioned under analytical properties. **Microcosmic salt**,  $\text{Na}(\text{NH}_4)\text{HPO}_4$ , is used in

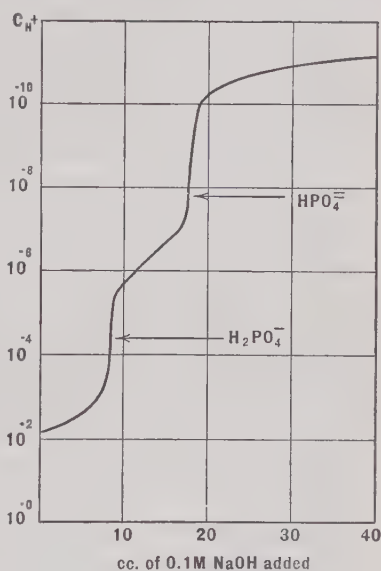


FIG 5. Titration curves for phosphoric acid.

bead tests similar to the borax bead. The **disodium phosphate**,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , is employed as a laboratory reagent. This compound loses water upon heating, forming, at about  $95^\circ$ , the anhydrous salt. Sodium and calcium diacid phosphates are used in one type of baking powder.

If the ortho-acid is heated to  $215^\circ$ , water is lost and **pyrophosphoric acid** is formed:  $2\text{H}_3\text{PO}_4 = \text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$ . When this acid is dissolved in cold water, the rate of transformation back into the ortho-acid is slow, but the transformation is rapid in hot water. All four hydrogen ions are replaceable by metals, and the four ionization constants are:  $K_1 = 1.4 \times 10^{-1}$ ,  $K_2 = 1.1 \times 10^{-2}$ ,  $K_3 = 2.9 \times 10^{-7}$ ,  $K_4 = 3.6 \times 10^{-9}$ . The silver salt,  $\text{Ag}_4\text{P}_2\text{O}_7$ , is but slightly soluble, and the magnesium salt,  $\text{Mg}_2\text{P}_2\text{O}_7$ , is of analytical importance. Sodium pyrophosphate is readily formed upon heating disodium hydrogen phosphate,  $\text{Na}_2\text{HPO}_4$ . The pyro-acid may be distinguished from the other phosphoric acids through the formation of a precipitate with zinc acetate.

**Metaphosphoric acid**,  $\text{HPO}_3$ , called glacial phosphoric acid is formed as a transparent glass by strongly igniting either the ortho- or pyro-acid. Like the pyro-acid, it is transformed but slowly into the ortho-acid in cold water. Most metaphosphates are insoluble, and the acid may be distinguished from the other phosphoric acids by the fact that it gives a precipitate with calcium ion.

**Tetraphosphoric acid**,  $\text{H}_6\text{P}_4\text{O}_{13}$ , is now a commercial product. It is used in reactions where a high  $\text{P}_2\text{O}_5$  content is desired. See also the use of  $\text{Na}_6\text{P}_4\text{O}_{13}$  as a water softener (V—11).

**55. The Peroxyphosphoric Acids.**— $\text{H}_3\text{PO}_5$  and  $\text{H}_4\text{P}_2\text{O}_8$  (compare Peroxysulfuric Acid), are formed by the electrolysis of solutions of the salt,  $\text{K}_2\text{HPO}_4$ , containing a little potassium fluoride and dichromate. The former is the principal product at high current density and the latter at lower current densities. The former may also be prepared by

treating the pentoxide with cold 30 per cent hydrogen peroxide.

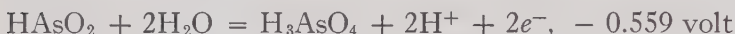
**56. Oxides and Acids of Arsenic.**—The **trioxide**,  $\text{As}_2\text{O}_3$ , ( $\text{As}_4\text{O}_6$ ), generally known as **white arsenic**, is commercially the most important compound of the element (cf. Fig. 3). Its most important source is the flue dust of smelters roasting arsenic-containing ores, and it is recovered from the dust by resubliming. The vapor condenses to a vitreous form which slowly changes to an octahedral crystalline modification. A monoclinic form may be prepared by heating for some time at  $200^\circ$ . The oxide is slightly soluble in cold water and more soluble in hot water. The rate of solution in both cases is very slow. The solution contains **arsenious acid**,  $\text{HAsO}_2$ . The acid is but slightly ionized,  $K = 6 \times 10^{-10}$ . About 60 per cent of the white arsenic consumed in the United States (40,000 tons per annum) is used in the manufacture of insecticides, 25 per cent in the manufacture of weed killers, and about 5 per cent in the manufacture of glass. Smaller quantities are used in the preparation of ant paste and rodent poison, as a mordant in dyeing, and as a wood preservative. The fatal dose of the oxide is 0.06–0.2 g., but a toleration may be developed that will permit the consumption of several times this amount without harmful effects. A number of organic arsenic compounds are used in medicine, which are highly toxic to lower organisms, but which can be tolerated in fairly large quantities by the human body.

Although the trioxide is somewhat amphoteric, it is more acidic than basic and dissolves readily in alkalis forming **arsenites**. Salts of the types  $\text{Na}_3\text{AsO}_3$ ,  $\text{NaAsO}_2$ , and  $\text{Na}_2\text{As}_4\text{O}_7$  may be obtained, but the free poly-acids are not stable and decompose to give the oxide. The soluble salts are highly hydrolyzed, due to the weakness of the acid. Ferric and magnesium arsenites are very slightly soluble, and suspensions of the hydroxides of these ions are administered in cases of arsenic poisoning. Sodium arsenite is used

extensively in the preparation of poison bait for grasshoppers, crickets, beetles and as a weed killer. A number of copper arsenites are important insecticides and pigments, such as **Paris green**,  $\text{Cu}_4(\text{C}_2\text{H}_3\text{O}_2)_2(\text{AsO}_3)_2$ , and **Scheele's green**,  $\text{CuHAsO}_3$ .

The trioxide dissolves in concentrated hydrochloric acid to form a **trichloride**, but this compound is completely hydrolyzed in dilute acid solution.

Arsenious acid may be oxidized to arsenic acid:



As is evident from the potential value, a fairly strong oxidizing agent is required. In neutral solution the reaction with iodine is quantitative, but in acid solution, the reaction is reversed and arsenic acid oxidizes iodide quantitatively. A value of  $-0.234$  volt is given in Table XII for the metal-arsenite couple.

**57. Orthoarsenic acid** is obtained upon evaporating a solution made by dissolving the trioxide in nitric acid. It crystallizes as  $2\text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$ . When heated, water is lost to form the pentoxide,  $\text{As}_2\text{O}_5$ , which readily dissolves again in water to form the acid.

Arsenates resemble the phosphates in solubility and crystalline form. The sodium salts,  $\text{Na}_2\text{HAsO}_4$  and  $\text{Na}_4\text{As}_2\text{O}_7$ , are used in the preparation of the **lead arsenates**,  $\text{Pb}_3(\text{AsO}_4)_2$  and  $\text{PbHAsO}_4$ , and the corresponding **calcium arsenates**. The former are employed extensively to provide protection against fruit insects, and the latter for controlling the cotton boll weevil. The value of arsenic as an oxidizing agent has been discussed above.

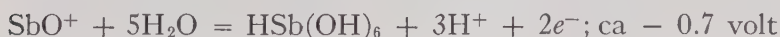
**58. Oxides and Acids of Antimony.**—The so-called **trioxide**,  $\text{Sb}_2\text{O}_3$  (or  $\text{Sb}_4\text{O}_6$ ), together with some tetroxide, is formed when antimony burns in air. The tetroxide may be prepared from the trioxide by heating in air to moderate temperature ( $300\text{--}400^\circ$ ), but at higher temperatures (about  $900^\circ$ ) it decomposes again to the trioxide. The trioxide is

amphoteric. It dissolves in concentrated acids, but only basic salts can ordinarily be crystallized from the solutions, e.g.  $(\text{SbO})_2\text{SO}_4$ ,  $(\text{SbO})\text{NO}_3$ , and  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$ . In hot water, these salts are completely hydrolyzed. The basic radical,  $\text{SbO}$ , is known as **antimonyl**, and the potassium antimonyl tartrate has long been used in medicine under the name of **tartar emetic**. The antimonyl ion gives only a very small concentration of  $\text{Sb}^{+++}$ .

The trioxide dissolves in alkalis, forming salts of **antimonous acid**. The sodium metaantimonite,  $\text{NaSbO}_2 \cdot 3\text{H}_2\text{O}$ , may be crystallized from the solution in sodium hydroxide. Salts of the ortho- and pyro-acids are also known.

The **tetroxide** is acidic in properties, dissolving in alkalis, but not acids. Two **hypoantimonates** occur as minerals,  $\text{CaSb}_2\text{O}_5$  and  $\text{CuSb}_2\text{O}_5$ .

**Antimony pentoxide**, like the corresponding oxide of arsenic, may be prepared by the action of nitric acid upon the trioxide. Antimonic acid appears to have the formula  $\text{HSb}(\text{OH})_6$ . The oxide and acid are only slightly soluble in water, but they dissolve easily in alkali. The so-called potassium acid pyroantimonate, probably  $\text{KSb}(\text{OH})_6$ , is very soluble in water, but the corresponding sodium compound is the least soluble of all sodium salts, and is sometimes employed as a test for sodium. As the solubility is about 0.03 g. per liter, the test is not delicate. The acid is a good oxidizing agent:



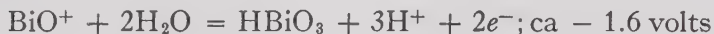
**59. Bismuth Oxides, Hydroxides, and Acids.**—Bismuth monoxide is prepared by heating basic bismuth oxalate:  $(\text{BiO})_2\text{C}_2\text{O}_4 = 2\text{BiO} + 2\text{CO}_2$ . It is readily oxidized to the **sesquioxide**. The latter oxide occurs in nature, and may be formed upon heating the metal in air. It has a yellow color, a comparatively high melting point, and exists in several crystalline modifications. This oxide is not soluble in bases but dissolves in acids, and normal salts may be obtained by



evaporating the acid solutions. When treated with water in the absence of acid, these salts are hydrolyzed to basic compounds, e.g., **basic nitrate** (also called subnitrate),  $\text{Bi}(\text{OH})_2\text{NO}_3$ , **basic sulfate**,  $(\text{BiO})_2\text{SO}_4$ , and **oxychloride**,  $\text{BiOCl}$ . A number of **basic carbonates** are known. These, and also the basic nitrate, are employed in medicine in the treatment of infections of the alimentary canal. The **hydroxide**,  $\text{BiOOH}$ , is precipitated from the salt solutions by alkalis. It is not soluble in excess of the reagent. Bismuthyl ion is readily reduced to the metal:



**60. Bismuth pentoxide**,  $\text{Bi}_2\text{O}_5$ , is formed by the action of very strong oxidizing agents upon the trioxide, e.g.  $\text{NaClO}$  in weakly alkaline solution. It is comparatively non-reactive. In concentrated sodium hydroxide it forms **sodium bismuthate**,  $\text{NaBiO}_3$ . In water or acid, this compound hydrolyzes to the acid, which is a very powerful oxidizing agent:



The acid will even oxidize manganous ion to permanganate in acid solution. Orthobismuthates are not known, although a tetroxide,  $\text{Bi}_2\text{O}_4$ , which is formed along with the pentoxide by the action of chlorine in alkaline solution upon the trioxide, is considered to be bismuth orthobismuthate,  $\text{Bi}(\text{BiO}_4)$ .

**61. Halogen Compounds.**—The various halogen compounds are summarized on page 229.

The halides may, in general, be prepared by the direct action of the elements. The compounds,  $\text{AsX}_3$ ,  $\text{SbX}_3$ , and  $\text{BiX}_3$ , may also be prepared by treating the corresponding oxide with the concentrated halogen acid. The relatively unstable  $\text{PCl}_2$  is formed by passing an electric spark through mixtures of  $\text{PCl}_3$  vapor and hydrogen.



TABLE XVI  
HALIDES OF PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH  
X = any halogen

P	As	Sb	Bi
PCl <sub>2</sub> , PI <sub>2</sub> PX <sub>3</sub>	AsI <sub>2</sub> AsX <sub>3</sub>	SbX <sub>3</sub> SbCl <sub>4</sub> in Rb <sub>2</sub> SbCl <sub>6</sub>	BiCl BiCl <sub>2</sub> , BiBr <sub>2</sub> BiX <sub>3</sub> BiCl <sub>4</sub>
PX <sub>5</sub> (except I)	AsF <sub>5</sub>	SbX <sub>5</sub> (except I)	BiF <sub>5</sub>

The salt-like nature of the compounds increases with the increasing size of the elements of the group; thus phosphorus trichloride is a non-conductor of electricity, while molten bismuth trichloride conducts readily. The halides are hydrolyzed by water, e.g.,  $\text{PCl}_5 + 4\text{H}_2\text{O} = \text{H}_3\text{PO}_4 + 5\text{HCl}$ . Often an oxyhalide forms as the first step, e.g.,  $\text{POCl}_3$ ,  $\text{SbOCl}$ , and  $\text{BiOCl}$ . The more basic the oxide, the less is the tendency of the halide toward hydrolysis: thus the hydrolysis of antimony and bismuth trichloride at ordinary temperatures stops at the oxychloride, and the reaction is readily reversed by acid. On account of its ready hydrolysis, phosphorus trichloride is used extensively in organic chemistry to replace hydroxide by chloride, e.g.  $3\text{CH}_3\text{CO}\cdot\text{OH} + \text{PCl}_3 = 3\text{CH}_3\text{COCl} + \text{H}_3\text{PO}_3$ . Antimony trichloride early received the name of **butter of antimony** and was employed for medicinal purposes. It was prepared by the reaction:  $\text{Sb}_2\text{S}_3 + 3\text{HgCl}_2 = 3\text{HgS} + 2\text{SbCl}_3$ . Bismuth triiodide is soluble in excess iodide, forming salts of the complex iodide  $\text{BiI}_4^-$ . The antimony tetrachloride is known only in complex salts.

**62. Sulfides.**—The following sulfides are known:

P	As	Sb	Bi
	AsS		BiS
P <sub>4</sub> S <sub>3</sub> P <sub>2</sub> S <sub>3</sub>	As <sub>2</sub> S <sub>3</sub>	Sb <sub>2</sub> S <sub>3</sub> Sb <sub>2</sub> S <sub>4</sub> Sb <sub>2</sub> S <sub>5</sub>	Bi <sub>2</sub> S <sub>3</sub>
P <sub>2</sub> S <sub>5</sub> PS <sub>6</sub>	As <sub>2</sub> S <sub>5</sub>		

The **sulfides of phosphorus** may be prepared by heating together the elements in equivalent amounts. Only two of the compounds,  $P_2S_5$  and  $P_4S_3$ , are sufficiently stable to be crystallized from solution in carbon disulfide. The pentasulfide is used as a reagent in organic chemistry. The trisulfide,  $P_4S_3$ , has been mentioned in connection with the manufacture of matches.

**Arsenic monosulfide**,  $AsS$ , occurs as the mineral **realgar**. It may be formed by heating together the elements, or by the reaction:  $FeS_2 + FeSAs = 2FeS + AsS$ . The yellow trisulfide,  $As_2S_3$ , also occurs as a mineral, **orpiment**. It is precipitated from solutions of arsenites by hydrogen sulfide. With pure arsenious acid, the precipitate is colloidal, but is coagulated by hydrogen ion or other positive ions. The sulfide is not soluble in concentrated hydrochloric acid. The sulfide is acidic in nature and dissolves in excess sulfide ion, forming **thioarsenite**:  $As_2S_3 + 3S^{--} = 2AsS_3^{---}$ . In polysulfide, it is oxidized to **thioarsenate**:  $As_2S_3 + 2S_2^{--} + S^{--} = 2AsS_4^{---}$ . The yellow trisulfide changes to a red form at  $170^\circ$ . The pentasulfide,  $As_2S_5$ , is formed by passing hydrogen sulfide into an acid solution of an arsenate. It is soluble in sulfide ion, forming the thioarsenate:  $As_2S_5 + 3S^{--} = 2AsS_4^{---}$ , and is reprecipitated from this compound by acid. The sulfide is not very stable and decomposes rather easily into the trisulfide and sulfur.

The mineral **stibnite**,  $Sb_2S_3$ , is black, but the antimony trisulfide, precipitated from solutions of the trichloride or antimonites, is orange red. It is soluble in concentrated hydrochloric acid, but not in dilute. It dissolves in sulfide and polysulfide, forming **thioantimonites** and **thioantimonates**, similar to arsenic trisulfide. When the thioantimonates are acidified, the **tetrasulfide** and sulfur are precipitated:  $2SbS_4^{---} + 6H^+ = Sb_2S_4 + S + 3H_2S$ . The tetrasulfide forms a mixture of thioantimonite and thioantimonate with excess sulfide ion, and is soluble in concentrated acid.

Black **bismuth sesquisulfide** is formed by heating together the element or by the action of hydrogen sulfide upon bismuth salts. It is not soluble in dilute hydrogen ion, but is dissolved by hot dilute nitric acid with the oxidation of the sulfur. It is not soluble in sulfide or polysulfide.

**63. Metal Compounds.**—Phosphides may be prepared (1) by heating together phosphorus and the finely divided metal or, (2) metal oxide; or by the action of (3) phosphorus, or (4) phosphine upon solutions of metal salts. Examples of (1) are  $\text{Hg}_3\text{P}_4$ ,  $\text{MnP}_2$ ,  $\text{Sn}_3\text{P}$  (used in phosphor bronze),  $\text{K}_2\text{P}_5$ ,  $\text{PbP}_5$ ; (2)  $\text{Ca}_3\text{P}_2$ ; (3)  $\text{Ag}_3\text{P}$ ,  $\text{Cu}_3\text{P}_2$  and (4)  $\text{Hg}_3\text{P}_4$ ,  $\text{Cu}_2\text{P}$ .

Arsenic unites with almost all metals at red heat, e.g.,  $\text{CoAs}_2$ ,  $\text{FeAs}_2$ ,  $\text{Fe}_4\text{As}_3$ ,  $\text{NiAs}$ ,  $\text{MnAs}$ . Antimony forms a series of compounds with an apparent oxidation state  $-2$ , e.g.,  $\text{CuSb}$ ,  $\text{NiSb}$ ,  $\text{ZnSb}$ ,  $\text{PtSb}_2$ ; and also compounds of the  $-3$  state, e.g.,  $\text{Ag}_3\text{Sb}$ ,  $\text{Mg}_3\text{Sb}_2$ ,  $\text{Cd}_3\text{Sb}_2$ ,  $\text{Fe}_3\text{Sb}_2$ . Bismuth also forms a number of metal compounds, e.g.,  $\text{Mg}_3\text{Bi}$ , although not so many as antimony.

#### ANALYTICAL

**64.** Phosphorus compounds are usually detected and determined as phosphate, since nitric acid readily oxidizes all of the lower states to this ion. In the absence of heavy metals whose phosphates are insoluble in ammonia, the phosphates may be precipitated as magnesium ammonium phosphate,  $\text{MgNH}_4\text{PO}_4$ , by a solution of magnesium chloride, ammonium hydroxide, and ammonium chloride. In quantitative determinations, this is ignited and weighed as  $\text{Mg}_2\text{P}_2\text{O}_7$ . Ordinarily the phosphate is precipitated in dilute nitric acid as the ammonium phosphomolybdate:  $\text{H}_3\text{PO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 21\text{HNO}_3 = (\text{NH}_3)_2\text{PO}_4 \cdot 12\text{MoO}_3 + 21\text{NH}_4\text{NO}_3 + 12\text{H}_2\text{O}$ . This precipitate is usually not weighed as such but is (1) dissolved in ammonium hydroxide and the phosphate reprecipitated as  $\text{MgNH}_4\text{PO}_4$  or (2) titrated with standard hydroxide:  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$

+  $23\text{OH}^- = \text{HPO}_4^{--} + 3\text{NH}_4^+ + 12\text{MoO}_4^{--} + 11\text{H}_2\text{O}$ . A colorimetric determination of phosphate is based upon the fact that the  $\text{MoO}_3$  in the phosphomolybdate is reduced to molybdenum blue much more readily than is a solution of molybdic acid. The reducing agent employed is benzi-dine or stannous chloride. Advantage may be taken of the slight solubility of bismuth phosphate,  $\text{BiPO}_4$ , to remove phosphate from acid solution. This is desirable in qualitative analysis since the presence of phosphate results in the precipitation of many slightly soluble compounds, e.g.,  $\text{CaHPO}_4$ , when  $\text{NH}_4\text{OH}$  is added.

Arsenic, antimony, and bismuth are usually detected by precipitation as sulfides in dilute acid solution. The properties of these compounds have been discussed, and the systematic scheme of separation (Append. VI) should also be consulted for the outline of the analysis. Arsenic is sometimes determined quantitatively as the ammonium arsenomolybdate similar to phosphate given above. It is more often determined by the oxidation of arsenite to arsenate in the presence of bicarbonate by iodine. Antimony may likewise be determined by the oxidation of antimonite to antimonate by iodine in alkaline solution, or better by the reduction of antimonie acid by iodide in acid solution. Bismuth may be precipitated and weighed as the oxychloride,  $\text{BiOCl}$ , or precipitated as the hydroxide and weighed as the trioxide.

Small quantities of arsenic and antimony are determined by the **Marsh test**, in which arsine and stibine are formed by reduction with zinc in hydrochloric acid, and the mixture of the gases with hydrogen passed into silver nitrate solution. Any antimony present is precipitated as silver antimonide, while the arsine is oxidized to arsenious acid. Upon filtering, the arsenic is confirmed in the filtrate by reprecipitation as sulfide, while the antimony in the precipitate is dissolved in hot concentrated tartaric acid and then reprecipitated as the sulfide. The test for arsenic may be modi-

fied by first separating the arsenic from the antimony by volatilizing the former as  $\text{AsCl}_3$  from a hydrochloric acid solution, and then, after reduction with zinc, detecting the arsine by placing a strip of paper wet with copper sulfate solution in the stream of gas. From the depth of color of the copper arsenide formed on the paper, the quantity of arsenic may be estimated. The method is capable of detecting 0.001 milligram of arsenic.

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# Chapter XII

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## SULFUR, SELENIUM, AND TELLURIUM

1. The relation of the three elements, sulfur, selenium, and tellurium to oxygen has been discussed in Chapter II. The outstanding characteristics of these elements is the six valence electrons and the tendency to add two more electrons to complete the octet. Thus the members of the group all form compounds with the electropositive elements, in which they exhibit an oxidation state of minus two, and with the more electronegative elements compounds in which the oxidation state varies from one to six, the most important of these being the + 4 and the + 6 states. The elements are all solids with relatively low melting points. Sulfur is distinctly a non-metal, but selenium and tellurium, especially the latter, show certain metallic properties. A marked characteristic of the group is the existence of a number of allotropic modifications. In addition to these three elements, the extremely rare, unstable, and highly radioactive element, polonium, belongs to this group. The few known facts relating to its chemical behavior are given in Chapter XXII.

2. **Occurrence.**—The amount of sulfur in the earth's crust is estimated at 0.1 per cent. Most of this occurs primarily as iron sulfide, but oxidation has given rise to large deposits of sulfate, chiefly of calcium and magnesium. The sulfides of all the heavy metals, except gold and platinum, occur as minerals, the most extensive deposits being those of iron pyrites,  $\text{FeS}_2$ . Free sulfur occurs in numerous



TABLE I  
ATOMIC AND PHYSICAL PROPERTIES

	S	Se	Te
Atomic number.....	16	34	52
Atomic weight.....	32.06	78.96	127.61
Isotopes.....	32, 33, 34, 36	74, 76, 77, 78, 80, 82	120, 122, 123, 124, 125, 126, 128, 130
Electrons in various quan- tum levels,			
1st.....	2	2	2
2d.....	8	8	8
3d.....	6	18	18
4th.....		6	18
5th.....			6
Density.....	R 2.07 M 1.96	G 4.80 R 4.50	6.24
Melting point, ° C.....	114.5	217	450
Boiling point, ° C.....	444.6	688	1390
Size of X <sup>++</sup> in crystals, cm. × 10 <sup>8</sup> .....	1.84	1.98	2.21

deposits, of special importance being those in Louisiana and Texas, and in Sicily.

Selenium and tellurium are much less abundant than sulfur, the estimated percentage in the igneous rocks being  $10^{-8}$  and  $10^{-9}$  respectively. The former occurs in the free state in most of the sulfur deposits, as selenides of many of the heavy metals, especially copper, silver, and lead; and less frequently selenites of copper, lead, cobalt, and other metals. Tellurium occurs chiefly as tellurides of copper, lead, silver, gold, iron, or bismuth. Tellurites and free tellurium are of rare occurrence.

### THE FREE ELEMENTS

**3. Sulfur.**—Sulfur vapor at the boiling point has a molecular weight of 230 and is mostly  $S_8$ , with some  $S_6$  and  $S_2$ . At  $1000^\circ$  it is largely  $S_2$  and at  $2000^\circ$  is about half dissociated into atomic sulfur. This tendency of sulfur to form complexes is a common characteristic of the group and may be attributed to the readiness with which a sulfur atom,  $\ddot{S}:$ ,

will share its electrons with other sulfur atoms in an effort to complete the octet. Liquid sulfur contains two molecular species called  $S_\lambda$  and  $S_\mu$  (probably  $S_8$  and  $S_6$ ), and

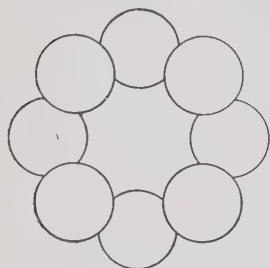


FIG. 1. Molecule of rhombic sulfur,  $S_8$ .

possibly one or two others. The structure of  $S_8$  is an eight membered ring with the S—S—S angle of  $105^\circ$ . The  $S_6$  is probably irregular chains. At  $120^\circ$  the equilibrium liquid contains 3.6 per cent  $S_\mu$  and at the boiling point 35 per cent. The heat of the transition is 416 calories. Such an equilibrium is probably not infrequent in liquids but the unusual fea-

ture with sulfur is the slowness with which the equilibrium state is reached. The time required is still further increased by the presence of traces of iodine or sulfuric acid, but is decreased by ammonia. Near the melting point sulfur is a light yellow mobile liquid; as the temperature is increased it becomes darker and more viscous with increasing content of  $S_\mu$ . The viscosity reaches a maximum around  $200^\circ$ , and falls off rapidly as the boiling point is approached.

Solid sulfur exists in two crystalline forms, rhombic and monoclinic, Fig. 2. There have been prepared, also, two other monoclinic, one triclinic and one rhombohedral form, but they are unstable with respect to the

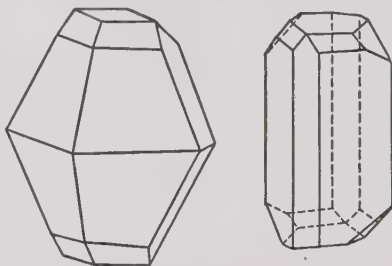


FIG. 2. Crystal forms of sulfur; sulfur rhombic (left) and sulfur monoclinic (right).

common forms. There are also a number of amorphous and colloidal forms whose characteristics doubtless depend chiefly upon the degree of dispersion. Rhombic sulfur is in equilibrium with monoclinic at  $96^\circ \text{C}$ . The reaction is rather slow, however, and by rapidly cooling sulfur, held for some

time just above its melting point, the long needle-shaped monoclinic crystals may be obtained. At room temperature they are transformed into rhombic in about a day. The heat of the transition is 70 cal. Rhombic sulfur melts at  $112.8^\circ$ , in equilibrium with  $S_\lambda$ , and at  $110.4^\circ$  to form the equilibrium mixture  $S_{\lambda\mu}$ . Monoclinic sulfur melts at  $119.2^\circ$  to form  $S_\lambda$  and  $114.5^\circ$  to form  $S_{\lambda\mu}$ . Both forms are soluble in  $CS_2$ . At  $25^\circ$  the solubility of the monoclinic is 1.28 times that of the rhombic. The molecular form of the solute in both cases is  $S_8$ . By heating sulfur near its boiling point, and suddenly cooling, a very plastic substance is obtained which consists of a mixture of rhombic crystals and an amorphous form not soluble in carbon disulfide. The latter form is essentially the super-cooled liquid. After some time it becomes very hard. The rate of change of the amorphous into the rhombic form requires years at ordinary temperature, but is rapid at  $90^\circ$ . There is at least one other amorphous modification, this form being soluble in carbon bisulfide. Finely divided sulfur prepared by precipitating sulfur from calcium polysulfide by the addition of acid is known as **milk of sulfur**, and finely divided sulfur formed by sublimation is known as **flowers of sulfur**.

The various forms of sulfur are all non-conductors of electricity and are insoluble in water.

4. The salt domes of Louisiana and Texas have now supplanted the mines of Sicily as the world's most important source of sulfur. These enormous domes consist of a salt core covered with a cap of gypsum, dolomite, and limestone

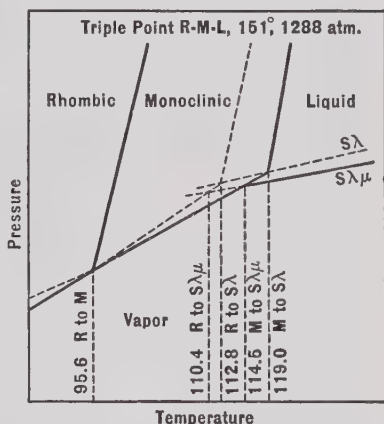


FIG. 3. Pressure-temperature diagram for sulfur; diagrammatic as actual vapor pressures are not known.

in which the sulfur occurs. It is extracted by the ingenious Frasch Process. Water heated to about  $180^{\circ}$  under pressure is pumped down bore holes and forced into the deposits; the sulfur is liquefied, and when a quantity of it collects at the bottom of the cavity it is forced to the surface by an air lift and discharged into bins. A small amount of sulfur is obtained from the purification of illuminating gas (Par. 8). The production of sulfur in the United States in 1937 was 2,740,000 tons. The major portion of this is made into sulfuric acid. Smaller amounts are consumed in the vulcanization of rubber, in the manufacture of sulfites and thiosulfates, in bleaching dried fruit, and for dusting and spraying plants.

Sulfur is both a fairly good reducing agent and oxidizing agent. It combines directly with all of the elements except gold, platinum, and the inert gases.

**5. Selenium.**—Selenium vapor at the boiling point consists of mixtures of  $\text{Se}_8$  —  $\text{Se}_2$ . The liquid also doubtless contains a number of molecular complexes but the problem has not been carefully investigated. The solid exists in three crystalline modifications, two of them rather similar monoclinic forms, red in color, soluble in carbon disulfide, and unstable with respect to the third form, a hexagonal rhombohedral structure known as metallic or grey selenium. The monoclinic forms are relatively stable below  $100^{\circ}$  and melt somewhat below  $200^{\circ}$ , the exact temperature being in doubt due to their rapid transformation, upon heating, into the grey form. The latter form melts at  $220^{\circ}$  and is insoluble in carbon bisulfide. Like sulfur, there is an amorphous modification, vitreous and black in color, which may be prepared by quickly cooling the liquid. Reduction of selenates results in the formation of two red modifications, one crystalline and the other amorphous. A number of colloidal forms of selenium have been prepared.

The electrical conductivity of the grey form is poor, but is greatly increased by light. This property makes selenium

useful in the construction of apparatus for the measurement of light intensity, as in photometers for measuring the intensity of radiation coming from the stars, and for the automatic turning of lights on and off at night and morning, respectively.

Large quantities of selenium could be recovered from the flues of the sulfur burners in sulfuric acid plants, and from the anode mud of electrolytic copper refineries. The free element has no extensive commercial applications. The largest consumption is in the glass works for making ruby red glass, and to neutralize the green color of glass, due to the presence of ferrous silicate. Some selenium is used in place of sulfur in the vulcanizing of certain types of rubber goods, and a small amount of selenium is added to copper alloys and stainless steel to make them more machinable.

The reactions of selenium are similar to those of sulfur, but the element is both a poorer reducing agent and a poorer oxidizing agent than sulfur, cf. Table II and Par. 13.

**6. Tellurium.**—The vapor of tellurium at the boiling point contains a much smaller per cent of the higher molecular complexes than in the case of sulfur and selenium, being mostly  $\text{Te}_2$ . The solid crystallizes in a silver white, semi-metallic, rhombohedral form, isomorphic with grey selenium, and in a second modification as yet little known. It may be precipitated in an amorphous modification by reduction and like the other members of the group readily forms various colloidal solutions. The amorphous form changes to the crystalline extremely slowly at ordinary temperatures, but rapidly just below the melting point. The metallic modification is insoluble in carbon bisulfide. Its density is 6.24. It is the poorest electrical conductor of any of the metals, specific resistivity being  $2 \times 10^{-1}$  ohm-cm. Tellurium with an atomic number of 52 has a higher atomic weight than iodine, atomic number 53. This situation arises through a preponderance of the heavier isotopes of tellu-

rium. Fairly large quantities of tellurium could be recovered from a number of metallurgical processes, especially the electrolytic copper refineries. Tellurium has been known as the useless metal; but its uses appear to be developing slowly. Like selenium it imparts free-cutting properties to steel. A 0.05 per cent alloy with lead increases the corrosion resistance of that metal.

**7. Hydrogen Compounds.**—The compounds,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ ,  $\text{H}_2\text{Te}$ , are much less polar liquids than water, as is indicated by their lower melting and boiling points. Their stability decreases and their power as reducing agents (Table II) increases with increasing atomic weight; that is, with increasing size of the atom, it becomes easier to pull off the two extra electrons. Hydrogen selenide and hydrogen telluride are endothermic. These compounds all possess very disagreeable odors and are extremely toxic.

TABLE II  
HYDROGEN COMPOUNDS OF SULFUR GROUP

	$\text{H}_2\text{S}$	$\text{H}_2\text{Se}$	$\text{H}_2\text{Te}$
Melting point, ° C.....	− 85.4	− 64	− 48
Boiling point, ° C.....	− 60.3	− 41.3	− 2.2
Heat of formation			
$\text{H}_2 + \text{X} = \text{H}_2\text{X (gas)}; \text{kcal.}$ .....	+ 5.3	− 18.5	− 34
Reduction potential			
$\text{H}_2\text{X (gas)} = \text{X} + 2\text{H}^+ + 2\text{e}^-, \text{in volts.}$ ...	− 0.14	+ 0.35	− 0.69

**8. Hydrogen Sulfide.**—Hydrogen sulfide may be formed by passing hydrogen into boiling sulfur, but is usually prepared by the action of acid upon a sulfide, particularly ferrous sulfide:  $\text{FeS} + 2\text{H}^+ = \text{Fe}^{++} + \text{H}_2\text{S}$ . The gas is soluble in water at 20° and 1 atm. to the extent of 290 volumes per 100 volumes of water. The resulting concentration is about 0.1*M*. In solution, it behaves as an extremely weak dibasic acid; the first ionization constant,  $\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$ , is  $1.15 \times 10^{-7}$ , and the second ionization constant,  $\text{HS}^- = \text{H}^+ + \text{S}^{--}$ ,  $1.0 \times 10^{-15}$ . The soluble



sulfides are, accordingly, highly hydrolyzed,  $0.1N$   $\text{Na}_2\text{S}$  containing about  $0.085N$   $\text{OH}^-$ . The acid sulfides or hydrosulfides, such as  $\text{NaSH}$ , are much less alkaline;  $0.1N$   $\text{NaSH}$  contains  $0.001N$   $\text{OH}^-$ . A saturated solution of  $\text{H}_2\text{S}$  in the presence of  $10^{-4}M$   $\text{H}^+$  has a sulfide ion concentration of  $10^{-15}M$ , and at  $0.3M$   $\text{H}^+$  the sulfide concentration is  $10^{-22}M$ . The concentration of sulfide in  $1M$   $(\text{NH}_4)_2\text{S}$  is  $10^{-6}M$ .

The sulfides of nearly all the metals except those of the main groups I, II, and III are insoluble in water. Extensive use is made in quantitative analysis of the varying degrees of solubility of the sulfides. Due to the weakness of hydrogen sulfide, the solubility of all sulfides is increased in acid. However, certain of the sulfides are so extremely insoluble that even large concentrations of hydrogen ion do not increase the solubility sufficiently to dissolve them in appreciable amounts. In general practice the metal sulfides are divided into two groups: (1) those precipitated in  $0.3N$   $\text{H}^+$  by  $\text{H}_2\text{S}$ , and (2) those not precipitated under these conditions. For details of the classification and separation, reference may be made to the general scheme of analysis, Appendix VI (cf. Hildebrand, *Prin. of Chem.*, p. 184).

Hydrogen sulfide burns in excess of air to form sulfur dioxide and water. In a limited amount of air, the free element is formed, as the dioxide and hydrogen sulfide react according to the equation:  $2\text{H}_2\text{S} + \text{SO}_2 = 3\text{S} + 2\text{H}_2\text{O}$ . Advantage is taken of the oxidation in a limited quantity of air to remove hydrogen sulfide from illuminating gas, where it is objectionable because of its odor and the corrosive nature of its combustion products, the process being carried out by admitting a small amount of oxygen and heating the mixture. The sulfur precipitated by the reaction is sold as a by-product.

Hydrogen sulfide tarnishes the surface of even such a noble metal as silver:  $2\text{Ag} + \text{H}_2\text{S} = \text{Ag}_2\text{S} + \text{H}_2$ . The action of hydrogen sulfide here as an oxidizing agent with the liberation of hydrogen is, of course, due to the great

stability of silver sulfide. The absorption of sulfur by the alkaline sulfides is discussed under the polysulfides.

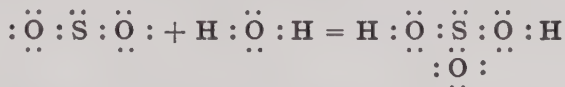
**9. Hydrogen Selenide and Telluride.**—The direct combination of hydrogen with selenium and tellurium shows less tendency to take place than with sulfur: however, the reactions do proceed to some extent at high temperatures. The compounds can be prepared, respectively, by the action of acid upon iron selenide or upon magnesium or aluminum telluride. They are gases with very disagreeable odors, and dissolve in water to form dibasic acids, probably slightly stronger than hydrogen sulfide. The selenides and tellurides of the heavy non-alkali metals are insoluble in water. The combustion reactions of these compounds are similar to hydrogen sulfide, but take place with greater energy (Table II). Hydrogen telluride decomposes rapidly above  $0^{\circ}$ .

**10. Oxides.**—Sulfur forms the oxides  $S_2O_3$ ,  $SO_2$ ,  $SO_3$ , and  $S_2O_7$ ; selenium only  $SeO_2$ ; and tellurium  $TeO$ ,  $TeO_2$ , and  $TeO_3$ . The slight tendency of selenium to form oxides is interesting in connection with the same characteristic of bromine, which occupies a position but one atomic number higher than selenium (cf. **XI—40**). The heat of formation of selenium dioxide is also less than either of the others, the values in kcals. being:  $SO_2$ (gas) 71,  $SeO_2$ (solid) 57, and  $TeO_2$ (solid) 87.

**11. Sulfur Sesquioxide.**—Sulfur reacts with concentrated sulfuric acid or with the trioxide to form the unstable solid sesquioxide,  $S_2O_3$ . It is not an acid anhydride, although its oxidation state corresponds to the hyposulfurous acid,  $H_2S_2O_4$ ; cf. Par. 24.

**12. Sulfur Dioxide and Sulfurous Acid.**—Sulfur dioxide is a gas condensing to a liquid at  $-10^{\circ}$ . It is formed by the oxidation of sulfur or sulfides, and by the reduction of sulfuric acid:  $S + O_2 = SO_2$ ;  $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$ ;  $2H_2SO_4 + Cu = CuSO_4 + SO_2 + 2H_2O$ . Due to the instability of sulfurous acid, the gas is liberated by the action

of strong acids upon sulfites:  $\text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{SO}_2 + \text{H}_2\text{O}$ . The gas is, however, moderately soluble in water, 50 volumes per unit volume of water at 20° and 1 atmosphere, forming sulfurous acid in solution. In terms of the electron structures, this reaction is:



Sulfurous acid is a rather weak dibasic acid, somewhat resembling carbonic acid. Its first ionization constant is 0.012 and the second  $1 \times 10^{-7}$ . Sulfurous acid is a fair oxidizing agent (Table III). It is unstable with respect to the decomposition:  $3\text{H}_2\text{SO}_3 = 2\text{SO}_4^{--} + 4\text{H}^+ + \text{S} + \text{H}_2\text{O}$ ; 0.33 volt. This reaction is slow but takes place under the influence of violet light and upon heating. Its most important reaction, however, is its oxidation to sulfuric acid (Table III). Many of its industrial uses depend upon this action as a reducing agent.

TABLE III  
OXIDATION-REDUCTION POTENTIALS OF SULFUROUS  
AND SULFURIC ACIDS

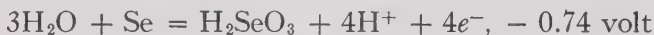
	VOLTS <sub>25°</sub>
$S + 3H_2O = H_2SO_3 + 4H^+ + 4e^-$ .....	- 0.45
$H_2SO_3 + H_2O = SO_4^{--} + 4H^+ + 2e^-$ .....	- 0.20

The alkali sulfites are but slightly hydrolyzed. The sulfites of many of the heavy metals are insoluble. The acid sulfites occur in two types, such as  $\text{NaHSO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_5$ , the latter being the anhydride of the former:  $2\text{HSO}_3^- = \text{S}_2\text{O}_5^{--} + \text{H}_2\text{O}$ .

At 20°, sulfur dioxide may be liquefied by a pressure of about 3 atmospheres. Because of its ease of liquefaction it is employed in refrigeration processes. The commercial product is usually sold as the liquid, in metal cylinders. Sulfurous acid has a powerful toxic action upon vegetable organisms, and thus finds many applications as a fungicide

and as a preservative in the preparation of beverages and foods. Sulfurous acid and sulfites are used extensively as bleaching agents for silk and woolen textiles, straw hats, feathers, and dried fruits. Sulfites have a digesting action upon wood, tending to separate the fibers as well as bleaching them, and their largest use is probably in the pulp and paper industry. Sulfur dioxide is also employed in petroleum refining.

**13. Selenium Dioxide and Selenites.**—The same general methods of preparing sulfur dioxide are applicable to selenium dioxide. This dioxide is a solid which sublims without melting. It has a characteristic odor which is described as that of "rotten horse-radish." It dissolves in water to form weak selenious acid,  $\text{H}_2\text{SeO}_3$ . Upon evaporating the solution, the free acid separates, and upon further heating, decomposes to the oxide. The acid is a much more powerful oxidizing agent than sulfurous acid:

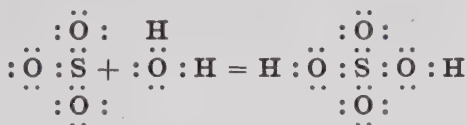


It thus oxidizes sulfurous acid to sulfuric:  $2\text{H}_2\text{SO}_3 + \text{H}_2\text{SeO}_3 = 4\text{H}^+ + 2\text{SO}_4^{--} + \text{Se} + \text{H}_2\text{O}$ . The selenium first separates as a red transparent colloid. When a solution of selenious acid is boiled with hydrogen bromide, the volatile tetrabromide escapes. Some attempts have been made to use the selenites as insecticides in fruit orchards, but they are so extremely toxic that they damage the growing plants.

**14. Tellurium Dioxide and Tellurites.**—Tellurium burns more readily than does selenium to form the dioxide. The dioxide is also formed by the action of other strong oxidizing agents upon the metal, and by reduction of tellurates. It does not unite readily with water but may be dissolved in alkali to form tellurites from which the slightly soluble acid may be obtained, upon acidifying, as a white solid. The oxide is somewhat soluble in acid,  $\text{TeO}_2 + \text{H}^+ = \text{TeO}_2\text{H}^+$ ,  $K = 8.9 \times 10^{-3}$ . The acid may also be obtained by the oxidation of tellurium by nitric acid. Salts of the "telluryl"

radical,  $\text{TeO}^{++}$ , or even  $\text{Te}_4\text{O}_7^{++}$  are known. With hydrogen iodide the acid forms the slightly soluble iodide,  $\text{TeI}_4$ . The acid forms a number of acid complexes of the general formula,  $\text{H}_2\text{TeO}_3 \cdot n\text{TeO}_2$ . The oxide (or acid) is a fair oxidizing agent but not so strong as selenous acid.  $2\text{H}_2\text{O} + \text{Te} = \text{TeO}_2 + 4\text{H}^+ + 4e^-$ ,  $-0.53$  volt. It is not easily oxidized to telluric acid. The dioxide forms, upon heating with tellurium, the **monoxide**,  $\text{TeO}$ . This oxide may also be formed by the hydrolysis of the chloride,  $\text{TeCl}_2$ .

**15. Sulfur Trioxide and Sulfuric Acid.**—Sulfur trioxide,  $\text{SO}_3$ , is a colorless liquid, freezing at  $15^\circ$  and boiling at  $46^\circ$ . The solid soon changes from a transparent glassy form to the polymer,  $\text{S}_2\text{O}_6$ , an opaque mass of needle shaped crystals which can be sublimed without melting. The trioxide possesses a remarkable affinity for water, forming sulfuric acid:



This reaction takes place with a hissing sound resulting from the large quantity of heat evolved, 38 kcal. The trioxide dissolves in concentrated sulfuric acid, forming the bi- or pyrosulfuric acid,  $\text{H}_2\text{S}_2\text{O}_7$ , called "fuming sulfuric acid" or "oleum."

**16. Contact Process.**—Sulfur trioxide is formed by the action of oxygen (air) or other powerful oxidizing agents upon sulfur dioxide. The reaction,  $\text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3$ , has, at  $25^\circ$  and partial pressures of 1 atm., a potential of 0.35 volt. Like many direct oxidations by  $\text{O}_2$ , this reaction is extremely slow. However, the rate can be increased by certain surface catalysts, including ferric oxide, vanadium pentoxide, and metallic platinum, the latter two being very effective. This catalysis is the basis for the "contact process" for the manufacture of sulfuric acid. The efficiency of platinum as a catalyst increases with temperature,



reaching a maximum about  $500^{\circ}$ , but the per cent of trioxide formed at equilibrium decreases at high temperature (Table IV).

TABLE IV  
EQUILIBRIUM CONSTANTS FOR THE REACTION,  $\text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3$

$t^{\circ}\text{C}.$ .....	300	527	680	790	900
$K$ .....	$8 \times 10^3$	28	3.6	1	0.38

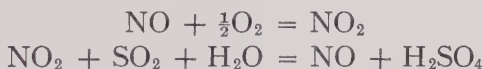
The reaction is generally carried out between  $380$  and  $450^{\circ}$  with excess air, under which conditions 97 to 99 per cent of the dioxide is converted into trioxide. The efficiency of the catalyst depends upon the extent of active surface. The platinum is obtained in a finely divided state by heating chlorplatinic acid,  $\text{H}_2\text{PtCl}_6$ , and is dispersed upon a base of asbestos fibers, magnesium sulfate, or silica gel. In recent years the cheaper vanadium pentoxide has replaced much of the platinum.

One of the factors in the successful operation of the process is the removal from the sulfur dioxide of all impurities which may "poison" the catalyst and render it inactive. It is particularly important to remove traces of solid sulfur, selenium dioxide, mercury, and compounds of phosphorus and arsenic. The sulfur trioxide formed by the reaction is more readily absorbed from the excess of oxygen by concentrated sulfuric acid than by water. The discovery of this curious fact aided materially in the development of the process. The explanation appears to be in the formation of a fog through the absorption of water vapor by the sulfur trioxide when water is used as the absorbing medium. The fog particles are small drops of sulfuric acid, and their thermal motion, compared with gas molecules, is very slow. With concentrated sulfuric acid, no fog is formed, and the rapidly moving sulfur trioxide molecules are more readily absorbed when the gas is bubbled through the acid. As the trioxide dissolves, water is added to keep the acid at



any desired concentration, usually at about 98 per cent acid. One of the mechanical problems is the temperature control. Since the reaction liberates heat, the temperature is kept from becoming too high by means of heat interchange between the incoming and outgoing gases. The reaction is carried out in cast iron containers, iron being insoluble (passive) in concentrated sulfuric acid.

**17. Lead Chamber Process.**—Many industries employ dilute sulfuric acid of no high degree of purity. It is cheaper to make this type of acid by the action of oxygen and steam upon sulfur dioxide, using nitric oxide as a catalyst. This process is known as the lead chamber process, from the large lead-lined reaction chambers employed. The presence of steam increases the ease of oxidation of sulfur dioxide,  $\text{SO}_2 + \text{O}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$ , 1.1 volts at  $25^\circ \text{C.}$ , as compared to 0.35 volt for the oxides. Although the various steps involved in the action of the gases with the catalyst are apparently quite complicated, the net result is that the nitric oxide acts as an oxygen carrier:



The reaction is carried out in immense lead chambers of approximately 200,000 cu. ft. capacity. The sulfuric acid condenses and is drained off at the bottom of the chamber. The nitrogen dioxide is recovered by passing the gas coming from the lead chamber through concentrated sulfuric acid. The probable reaction is:  $2\text{NO}_2 + \text{H}_2\text{SO}_4 = \text{SO}_2(\text{OH})(\text{NO}_2) + \text{HNO}_3$ . This reaction is reversed upon dilution; the nitric and nitrosyl sulfuric acid,  $\text{SO}_2(\text{OH})(\text{NO}_2)$ , again forming sulfuric acid and nitrogen dioxide. Advantage is taken of this reversal to restore the oxides of nitrogen to the system by diluting the nitrogen containing acid, and by passing the sulfur dioxide, which also aids in the reversal by removing  $\text{NO}_2$ , through the solution before entering the lead chambers. This is carried out in a large tower employ-

ing the counter current principle. Thus the nitrogen oxides are again restored to the chambers and at the same time the chamber acid is concentrated. The ordinary chamber acid is about 60 to 70 per cent sulfuric acid and large quantities are sold at these concentrations. Further concentration may be carried out by evaporating in lead pans until a concentration of 77 per cent is reached. Below this concentration the lead is not rapidly oxidized because of a protective layer of sulfate. Above this concentration, however, the sulfate is soluble, and the concentration process is usually continued in iron vessels. The use of silica and silicon iron containers for the further concentration is becoming more general.

Formerly a large fraction of the sulfur dioxide consumed in the manufacture of sulfuric acid in this country was made by roasting iron pyrites,  $\text{FeS}_2$ , but at present the major portion is made by burning sulfur. However, two thirds of the world's production of sulfuric acid is still made from pyrites. Some sulfur dioxide is utilized from the stacks of the copper, zinc, and lead smelters.

**18. Properties of Sulfuric Acid.**—The specific gravity of sulfuric acid solutions increases rapidly with concentration, becoming 1.85 for 100 per cent acid. The pure acid melts at  $10.5^\circ$ , but the melting point is greatly lowered by the presence of either water or sulfur trioxide. The boiling point is  $270^\circ$  at 755 mm., but is without special significance since the solution loses sulfur trioxide and changes in composition until the constant boiling mixture of 98.3 per cent sulfuric acid is reached at  $338^\circ$ . In addition to the compounds,  $\text{SO}_3 \cdot \text{H}_2\text{O}$ ,  $(\text{H}_2\text{SO}_4)$  and  $2\text{SO}_3 \cdot \text{H}_2\text{O}$ ,  $(\text{H}_2\text{S}_2\text{O}_7)$ , the freezing point curves, Fig. 4, indicate the hydrates,  $\text{SO}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{SO}_3 \cdot 3\text{H}_2\text{O}$ , and  $\text{SO}_3 \cdot 5\text{H}_2\text{O}$ . The great stability of these hydrates renders sulfuric acid an excellent dehydrating agent. The concentrated acid will remove water from cellulose,  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , and sugar,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , depositing carbon:  $\text{C}_{12}\text{H}_{22}\text{O}_{11} = 12\text{C} + 11\text{H}_2\text{O}$ . It, however, is not as

powerful a dehydrating agent as phosphorus pentoxide, since this oxide will liberate sulfur trioxide from sulfuric acid:  $\text{P}_2\text{O}_5 + \text{H}_2\text{SO}_4 = 2\text{HPO}_3 + \text{SO}_3$ . The heat of solution of sulfuric acid in a large amount of water is 19.0 kcal. Sulfuric acid is dibasic, the first ionization is complete, but the second ionization is somewhat weak, the constant being 0.012 at 25° C. At molal concentrations the potential of the acid as an oxidizing agent is not very great (Table III), but the energy of concentration is so large that the oxidizing power of the concentrated acid becomes very strong, sufficient to dissolve copper or silver.

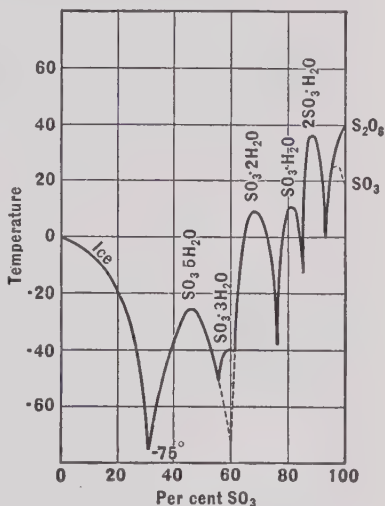


FIG. 4. The system sulfur trioxide and water.

TABLE V

CONSUMPTION OF SULFURIC ACID IN U. S. IN 1937  
(Tons of 62% Acid)

Fertilizers . . . . .	1,940,000
Metallurgical . . . . .	1,400,000
Petroleum . . . . .	1,200,000
Chemicals . . . . .	1,000,000
Coal products . . . . .	860,000
Paints and pigments . . . . .	525,000
Rayon and cellulose . . . . .	375,000
Explosives . . . . .	225,000
Textiles . . . . .	110,000

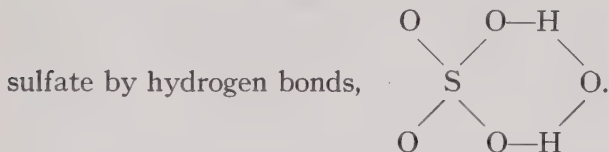
**19. Applications of Sulfuric Acid.**—The annual production of sulfuric acid in the United States is about eight million tons of 62 per cent acid. The distribution of this acid among the more important consuming industries is given in Table V. Sulfuric acid has played a leading role

in the industrial development of the past century, due to its low cost of production and various useful chemical properties. The **high boiling point** accounts for its use in displacing more volatile acids such as hydrochloric, hydrofluoric, and nitric acids from their salts. As a **strong acid**, it is used to convert calcium phosphate to acid phosphate for fertilizer, to dissolve base metals and oxides, to clean metal surfaces prior to galvanizing and tinning, and to neutralize ammonia in its recovery from coke ovens and the packing industries. As a **dehydrating agent**, it plays an essential role in the manufacture of explosives, celluloid, pyroxaline, varnishes, ether, etc. The nitration process liberates water which is removed by the sulfuric acid thus allowing the reaction to go to completion. Many of its applications depend upon the **oxidizing power** of the concentrated acid, e.g. in removing tars and organic sulfides from petroleum. The **insolubility of many sulfates** is another factor of industrial importance, as in the manufacture of the important pigment, lithophone, a mixture of barium sulfate and zinc sulfide.

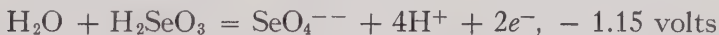
**Pyrosulfuric acid**,  $\text{H}_2\text{S}_2\text{O}_7$ , is used when the acid in its most powerful oxidizing and dehydrating form is desired. It was employed during the Great War to form "smoke screens," since it forms a very stable mist or fog composed of tiny drops of sulfuric acid.

**20. Sulfates.**—As a dibasic acid, sulfuric acid forms both neutral and acid salts. The acid salts may be dehydrated to form the pyrosulfates:  $2\text{NaHSO}_4 = \text{Na}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O}$ . The normal salts of the alkali and alkaline earth metals and lead do not readily decompose upon heating, but the sulfates of the nobler metals evolve sulfur trioxide, or sulfur dioxide and oxygen if the decomposition temperature is high. The decomposition of ferric sulfate was once an important method of preparing sulfur trioxide and sulfuric acid. Sulfates are reduced by heating with carbon to form the sulfide:  $\text{Na}_2\text{SO}_4 + 2\text{C} = \text{Na}_2\text{S} + 2\text{CO}_2$ . Barium and

lead sulfates are among the more important insoluble sulfates (Par. 32). Though insoluble in dilute acids, their solubility is increased in concentrated sulfuric acid by the slight weakness of the  $\text{HSO}_4^-$  ion. Many of the solid sulfates crystallize with an odd number of water molecules, e.g.,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . In this example four water molecules are attached to the copper and the fifth is attached to the



**21. Selenic Acid.**—Rather powerful oxidizing agents, such as  $\text{PbO}_2$  or  $\text{Cl}_2$ , are required to oxidize selenous to selenic acid, even in dilute solution:



Conversely, selenic acid, when concentrated, is a very powerful oxidizing agent, liberating chlorine from chloride, and dissolving gold, but not platinum unless chloride is present. The reaction is, however, slow with many reducing agents, e.g.  $\text{H}_2\text{S}$  and  $\text{SO}_2$ , but is faster in the presence of chloride. The free acid is easily prepared by the action of bromine upon silver selenite:  $\text{Ag}_2\text{SeO}_3 + \text{H}_2\text{O} + \text{Br}_2 = \text{H}_2\text{SeO}_4 + 2\text{AgBr}$ . The pure acid melts at  $58^\circ$  and its concentrated solution is thick and sirupy. When dehydrated, it gives selenous oxide and oxygen. The solubilities of the selenates are similar to the sulfates. The barium salt is easily confused with barium sulfate. The soluble selenates are, however, easily distinguished from sulfates by their higher oxidizing power.

**22. Tellurium Trioxide and Telluric Acid.**—Telluric acid forms salts of the types  $\text{Ag}_6\text{TeO}_6$  and  $\text{Ag}_2\text{TeO}_4$ . The acid,  $\text{H}_6\text{TeO}_6$ , is but sparingly soluble in water, and is but weakly acidic. Upon heating, it loses water to form  $\text{H}_2\text{TeO}_4$  and

then  $\text{TeO}_3$ . The trioxide does not react with water. The acid is a good oxidizing agent,



The ability of tellurium to hold more than the customary four oxygen atoms, as is shown in  $\text{H}_6\text{TeO}_6$ , is interesting in connection with the same property of iodine and antimony, which occupy the neighboring position in the periodic table.

**23. Other Sulfur Acids.**—A very large number of complex acids of sulfur exist,



Hyposulfurous acid

Thiosulfuric acid

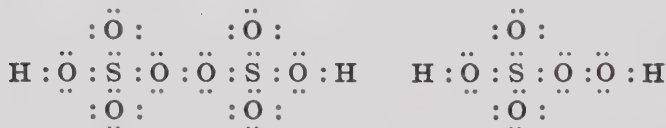
Hydrogen polysulfide



Dithionic acid

Trithionic acid

Tetrathionic acid



Peroxydisulfuric acid

Peroxymonosulfuric acid

due to the ability of the sulfur atom to share electrons with oxygen and with other sulfur atoms, as is illustrated by the structural formulas of a number of these acids given above. The behavior of sulfur is somewhat comparable to carbon in this tendency to form molecules of high molecular weight with oxygen and hydrogen. A few of the more important acids will be discussed.

**24. Hyposulfurous Acid.**—The zinc salt of hyposulfurous acid is formed by the reduction of sulfurous acid by zinc:  $2\text{H}_2\text{SO}_3 + \text{Zn} = \text{ZnS}_2\text{O}_4 + 2\text{H}_2\text{O}$ . A solution of the sodium



salt is prepared commercially from the zinc salt by the addition of sodium sulfite, as zinc sulfite is but moderately soluble. The salts are also prepared by the cathode reduction of bisulfite solution:  $2\text{H}_2\text{SO}_3 + 2e^- = \text{S}_2\text{O}_4^{--} + 2\text{H}_2\text{O}$ . The acid is too unstable to be prepared in the pure state. It is a very rapid reducing agent, reducing oxygen almost instantaneously,  $2\text{H}_2\text{O} + \text{HS}_2\text{O}_4^- = 2\text{H}_2\text{SO}_3 + \text{H}^+ + 2e^-$ , 0.23 volt. The sodium salt is employed commercially for the reduction of indigo to indigo white.

**25. Thiosulfuric Acid.**—Sulfites react with sulfur in alkaline solution to form thiosulfate:  $\text{SO}_3^{--} + \text{S} = \text{S}_2\text{O}_3^{--}$ . The free acid is unstable and the reaction is reversed by acid, sulfurous acid being formed and the sulfur precipitated. The reversal may be brought about even by weak acids: thus a sodium thiosulfate solution becomes turbid if exposed to the action of the carbonic acid of the air. The sulfur precipitated is amorphous and at first usually colloidal. The somewhat analogous oxidation of sulfide by sulfur in alkaline solution is discussed under the polysulfides. The product of that oxidation,  $\text{SS}_4^{--}$ , may be considered as the tetrathiosulfate.

Thiosulfate is oxidized ( $\text{S}_2\text{O}_3^{--} = \text{S}_4\text{O}_6^{--} + 2e^-$ , -0.15 volt) by iodine, ferric ion, and other moderately strong oxidizing agents to the tetrathionate. This extremely important reaction with iodine is discussed under that element (cf. **X—21**). More powerful oxidizing agents, such as chlorine and bromine, oxidize the thiosulfate to sulfate:  $5\text{H}_2\text{O} + \text{S}_2\text{O}_3^{--} + 4\text{Cl}_2 = 2\text{SO}_4^{--} + 8\text{Cl}^- + 10\text{H}^+$ . Thiosulfate forms complex ions and salts with many of the ions of the more noble metals, including  $\text{Ag}^+$ ,  $\text{Au}^{+++}$ ,  $\text{Cu}^+$ ,  $\text{Hg}^{++}$ ,  $\text{Pb}^{++}$ . Advantage is taken of this property in photography in the "fixing bath," to dissolve out the unchanged silver bromide.

Sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , called "**hypo**" from the older name "hyposulfite," is of considerable commercial importance. Besides its use in photography, it is em-

ployed in the textile and paper industries as an "antichlor" to remove the excess chlorine used in bleaching, and in certain metallurgical processes. The very unstable sulfoxylic acid,  $\text{H}_2\text{SO}_2$ , has the same oxidation state as the average value for the sulfur in thiosulfate and decomposes to give the latter,

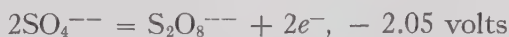


**26. Polysulfides.**—Soluble sulfides readily dissolve sulfur to form a series of compounds giving the ions,  $\text{S}_2^{--}$  to  $\text{S}_5^{--}$ . The alkaline solutions may be evaporated and the crystalline salts obtained, but the acids are unstable, forming hydrogen sulfide and free sulfur. These polysulfides act both as reducing and oxidizing agents. An example of the latter action is the oxidation of stannous sulfide to thio-stannate. Calcium polysulfide, made by dissolving sulfur in lime, the product thereby containing some thionic salts, is used extensively as an insecticide for vineyards and orchards.

**27. Thionic Acids.**—The structural formulas of a number of acids of the type,  $\text{H}_2\text{S}_n\text{O}_6$ , have been indicated above. The subscript varies from 2 to 5. These acids are analogous to the peroxyacids. Thus tetrathionic acid may be prepared by the anodic oxidation of thiosulfate,  $2\text{HS}_2\text{O}_3^- = \text{H}_2\text{S}_4\text{O}_6 + 2e^-$ , similarly to the preparation of peroxydisulfuric acid,  $\text{H}_2\text{S}_2\text{O}_8$ , from sulfuric acid; and the structure of the tetrathionate differs from that of persulfate only by the substitution of sulfur for the peroxygen. Dithionate may be prepared by the anodic oxidation of sulfite,  $2\text{SO}_3^{--} = \text{S}_2\text{O}_6^{--} + 2e^-$ . Mixtures of the acids result from the interaction of sulfurous and hydrosulfuric acid in solution:  $\text{H}_2\text{S} + 3\text{SO}_2 = \text{H}_2\text{S}_4\text{O}_6$ ;  $2\text{H}_2\text{S} + 6\text{SO}_2 = \text{H}_2\text{S}_3\text{O}_6 + \text{H}_2\text{S}_5\text{O}_6$ ;  $3\text{H}_2\text{S} + 9\text{SO}_2 = \text{H}_2\text{S}_2\text{O}_6 + 2\text{H}_2\text{S}_5\text{O}_6$ . The gases themselves react to form sulfur and water. The various acids or salts are formed as intermediate products in many oxidation-

reduction reactions involving sulfates and sulfites: thus, manganese dioxide reacts upon cold sulfurous acid to form manganese dithionate:  $\text{MnO}_2 + 2\text{H}_2\text{SO}_3 = \text{MnS}_2\text{O}_6 + 2\text{H}_2\text{O}$ . The acids are unstable in regard to decompositions giving sulfate, sulfite, and sulfur. The tetrathionate is the most important of these compounds. Its formation from thio-sulfate by the action of iodine and ferric ion has been discussed.

**28. Peroxysulfuric Acid.**—Two important acids and an oxide of sulfur containing peroxyoxygen are known. The oxide,  $\text{S}_2\text{O}_7$ , is formed in small amounts by an electrical discharge in a mixture of sulfur dioxide and oxygen:  $4\text{SO}_2 + 3\text{O}_2 = 2\text{S}_2\text{O}_7$ . It dissolves in sulfuric acid to form peroxydisulfuric acid,  $\text{H}_2\text{S}_2\text{O}_8$ . This acid, usually called persulfuric acid, may be prepared by the reaction between cold concentrated sulfuric acid and concentrated hydrogen peroxide:  $2\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 = \text{H}_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O}$ , or by the electrolysis of cold concentrated sulfuric acid:  $2\text{HSO}_4^- = \text{H}_2\text{S}_2\text{O}_8 + 2e^-$ . The sodium salt is prepared commercially by the electrolysis of concentrated solution of sodium acid sulfate. The sodium peroxydisulfate is but moderately soluble and crystallizes out. Peroxydisulfuric acid hydrolyzes in steps forming first the peroxymono-acid called "**Caro's acid**," and this hydrolyzes to form sulfuric acid and hydrogen peroxide:  $\text{H}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_5$ ;  $\text{H}_2\text{SO}_5 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ . The mono-acid may be prepared by the electrolysis of cold moderately concentrated sulfuric acid. Both of the acids evolve oxygen readily, but their salts are fairly stable. The sodium peroxydisulfate is of considerable commercial importance as an oxidizing agent:



In the presence of  $\text{Ag}^+$  as a catalyst, manganous ion is oxidized to permanganate by the acid. The action of silver

as a catalyst appears to involve the formation of  $\text{AgO}^+$  and  $\text{Ag}^{++}$ .

**29. Other Thio-acids.**—Sulfur may be substituted for oxygen in a number of acid radicals similar to its substitution in the sulfate radical, provided the radical is not such a powerful oxidizing agent that the sulfur is rapidly oxidized to higher valences. For example, compounds are prepared in which the oxygen in phosphate is replaced by sulfur, forming the series,  $\text{Na}_3\text{PO}_3\text{S}$  to  $\text{Na}_3\text{PS}_4$ . The strong analogy between sulfur and oxygen is well illustrated by the reaction of barium sulfide and carbon disulfide to give barium thiocarbonate,  $\text{BaS} + \text{CS}_2 = \text{BaCS}_3$ , similar to the formation of barium carbonate from the two oxides. Mention should also be made of **thiocyanic acid**,  $\text{HSCN}$ , as many of the salts of that acid are of considerable importance (cf. **XIII—26**).

**30. Sulfur Trioxide-ammonia Derivatives.**—Sulfur trioxide and ammonia react to form **amidosulfonic acid** (**sulfamic acid**),  $\text{NH}_2\text{SO}_3\text{H}$  and amidodisulfonic acid,  $\text{NH}(\text{SO}_3\text{H})_2$ . The two acids are also formed by heating urea with concentrated sulfuric acid. Sulfamic acid is used in the manufacture of dyes and cleaning compounds and in tanning. Its salts are valuable in flameproofing paper and textiles. **Sulfamide**,  $\text{SO}_2(\text{NH}_2)_2$ , is formed by the action of ammonia on sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$ .

**31. Other Acids of Selenium and Tellurium.**—The tendency to form long chain complicated acids, and the tendency to substitute for oxygen, exhibited by sulfur in the thio-acids, decrease with the heavier elements in the group. Both selenium and tellurium form salts of polyhydro acids, e.g.  $\text{NaSe}_2$ ,  $\text{NaTe}_3$ . Selenium forms an unstable peroxy-acid but tellurium does not. Selenium substitutes for oxygen in a number of acids and in many organic compounds, e.g.,  $\text{NaSeCN}$ , sodium selenocyanate.

**32. Halogen Compounds.**—The halogens combine with the elements sulfur, selenium, and tellurium to form nu-

merous compounds. These, together with a number of oxy-chlorides, compounds containing chlorine with oxygen and hydrogen, have been tabulated below:

S	Se	Te
SF <sub>6</sub> SF <sub>4</sub> SF <sub>2</sub> S <sub>2</sub> F <sub>2</sub> S <sub>2</sub> F <sub>10</sub> SCl <sub>4</sub> SCl <sub>2</sub> S <sub>2</sub> Cl <sub>2</sub> S <sub>2</sub> Br <sub>2</sub>	SeF <sub>6</sub> SeF <sub>4</sub> SeCl <sub>4</sub> Se <sub>2</sub> Cl <sub>2</sub> SeBr <sub>4</sub> Se <sub>2</sub> Br <sub>2</sub> SeI <sub>4</sub> Se <sub>2</sub> I <sub>2</sub> SeOCl <sub>2</sub> H <sub>2</sub> SeO <sub>2</sub> Cl <sub>2</sub> SeOBr <sub>2</sub>	TeF <sub>6</sub> TeF <sub>4</sub> TeCl <sub>4</sub> TeCl <sub>2</sub> TeBr <sub>4</sub> TeBr <sub>2</sub> TeI <sub>4</sub> TeI <sub>2</sub> TeOCl <sub>2</sub> H <sub>2</sub> TeO <sub>2</sub> Cl <sub>2</sub> H <sub>2</sub> TeCl <sub>6</sub>
SO <sub>2</sub> Cl <sub>2</sub> SOCl <sub>2</sub> HSO <sub>3</sub> Cl S <sub>2</sub> O <sub>5</sub> Cl <sub>2</sub>		

In general, the halogen compounds hydrolyze with water to form the hydrogen halide and the acid of the positive element. The latter may, however, be unstable in respect to decomposition into compounds of higher and lower oxidation states.

The most important of these compounds is **sulfur monochloride**, S<sub>2</sub>Cl<sub>2</sub>. This is formed by the direct action of chlorine upon hot sulfur. It is a reddish yellow liquid and an excellent solvent for sulfur. For this reason, it is used in vulcanizing rubber. It is hydrolyzed by water:  $2S_2Cl_2 + 2H_2O = SO_2 + 4HCl + 3S$ . The other two chlorides may be formed by the action of chlorine upon cold monochloride, but are decomposed by gentle heating.

Sulfur dioxide reacts with chlorine, forming **sulfuryl chloride**, SO<sub>2</sub>Cl<sub>2</sub>. **Thionyl chloride**, SOCl<sub>2</sub>, results from the reduction of phosphorus pentachloride by sulfur dioxide:  $PCl_5 + SO_2 = SOCl_2 + POCl_3$ . **Chlorosulfuric acid**, HSO<sub>3</sub>-Cl, is formed by the direct union of sulfur trioxide and hydrogen chloride. **Pyrosulfuryl chloride**, S<sub>2</sub>O<sub>5</sub>Cl<sub>2</sub>, is formed by the direct union of sulfur trioxide and sulfuryl chloride.

**33. Selenium and Tellurium with Sulfur.**—There appear to be no compounds containing selenium and sulfur only, and the two elements form several series of mixed crystals. The precipitate obtained by passing hydrogen sulfide into



tellurous acid appears to be a mixture of the free elements and the sulfide  $\text{TeS}_2$ .

Concentrated sulfuric acid dissolves both selenium and tellurium with the formation of the compounds,  $\text{SeSO}_3$  and  $\text{TeSO}_3$ , respectively, analogous to  $\text{S}_2\text{O}_3$  (Par. 11).

Selenium may be substituted for sulfur in certain of the complex sulfur acids, e.g. seleno sulfuric acid,  $\text{H}_2\text{SSeO}_3$ .

**34. Analytical.—Sulfur.** The free element may be recognized by the pungent odor of sulfur dioxide upon burning; or by dissolving in hot alkali solution and placing a drop of the solution on a silver coin, a black stain,  $\text{Ag}_2\text{S}$ , indicating the presence of sulfur. Sulfides are detected by the liberation of hydrogen sulfide by dilute acids, which may be recognized by its odor, or by its reaction with moist lead acetate paper. Sulfates are detected by the precipitation of barium sulfate, which is not soluble in dilute acids. Since sulfur in the lower valences is readily oxidized to sulfate, this also constitutes a general method for the detection and estimation of sulfur. Thus in quantitative analysis, sulfur is usually precipitated and weighed as barium sulfate. Due to the occlusion of soluble salts by the barium sulfate, it is difficult to obtain the precipitate pure. This error is decreased by precipitating from a large volume, since the occlusion is proportional to the concentration of the soluble salts, and also by digesting the precipitate for some time, which allows the more soluble small crystals to dissolve and slowly recrystallize out on the larger crystals. If precipitated from cold concentrated solution, barium sulfate is so finely dispersed that it cannot be retained by ordinary filter paper.

**Selenium.** The free element dissolves in concentrated sulfuric acid to form a green solution,  $\text{SeSO}_3$ . In the ordinary scheme of analyses, selenates are precipitated by hydrogen sulfide as elementary selenium, which is soluble in ammonium polysulfide. Red selenium is precipitated from cool selenous acid solution by strong reducing agents, hydroxylamine hydrochloride,  $\text{NH}_2\text{OHHCl}$ , being often



employed. The precipitate turns black upon heating. A separation of selenium, arsenic, and germanium from the other elements may be made by distilling the material in solution with  $\text{HBr}$  and  $\text{Br}_2$ . The distillate consists of  $\text{SeBr}_4$ ,  $\text{H}_3\text{AsO}_4$ , and  $\text{GeBr}_4$ .

In quantitative analysis, the selenium may be precipitated and weighed as the element, or determined volumetrically with oxidizing or reducing agents through the selenous-selenic acid couple.

**Tellurium.** Tellurium resembles selenium in its precipitation with hydrogen sulfide. The two elements may be separated by the hydrogen bromide treatment (cf. above) or by the reactions of the tetravalent acids with iodide in dilute acid, selenium precipitating as the red element, and tellurium forming a black precipitate,  $\text{TeI}_4$ , soluble in excess iodide to give a red solution of  $\text{TeI}_6^{--}$ . Tellurium may be weighed quantitatively as the metal or the dioxide. Tellurous acid may be oxidized by permanganate quantitatively to telluric acid.

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# Chapter XIII

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## CARBON

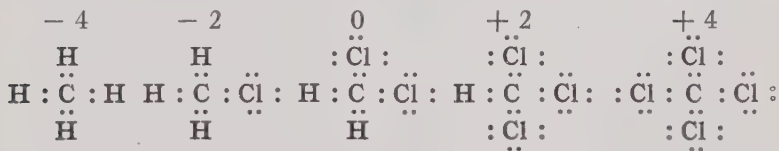
1. Several hundred thousand compounds of carbon are known, and the properties and reactions of these compounds constitute such a large portion of chemical knowledge that the whole of the science is now generally considered in respect to two great subdivisions, **organic chemistry** dealing with the carbon compounds, and **inorganic chemistry** dealing with the compounds of all the other elements.

It was once felt that the structure of the carbon compounds differed in some fundamental respect from that of the compounds of other elements, but it is now realized that their constitution can be correlated with the structure of the carbon atom and with the same general principles of compound formation which have been discussed in connection with the other periodic groups. This chapter will deal briefly with the structure of organic compounds in general and with the properties of the oxides and simpler carbon compounds. The relation of carbon to the other members of Group IV will be considered in the two subsequent chapters.

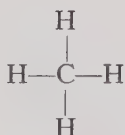
2. **Structure of Carbon Compounds.**—Carbon forms compounds in which the oxidation state varies from  $-4$  to  $+4$ . However, the assignment of oxidation states in most of its compounds is so arbitrary as to be of little significance, that is, although we know the total number of valence electrons in the molecule, we are unable to say that a given number of electrons are definitely associated with a

certain atom. The carbon atom, having four electrons, occupies a position intermediate to the elements which, on one side, lose their electrons to form positive ions, and on the other side add electrons to complete the octet and thus form negative ions. As a consequence of this position, it forms compounds in which it appears to complete the octet by sharing its electrons with other atoms. In terms of the idea that the pair of electrons constitutes a chemical bond, the behavior of carbon may be summarized by the statement: **carbon tends to form compounds in which it shares four pairs of electrons with the surrounding atoms.** The four bonds are arranged in tetrahedral symmetry, the carbon atom being at the center and the four attached atoms at the corners of the tetrahedron. As an illustration of this statement and of the non-polar character of the bonds, the electron formulas of the simple carbon, hydrogen, chlorine compounds are given below (cf. also Hildebrand, *Prin. of Chem.*, p. 279).

*Oxidation State:*

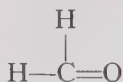


This idea of the four bonds of carbon has been of the greatest importance in the development of organic chemistry, and it is customary to represent these bonds by lines, e.g.,

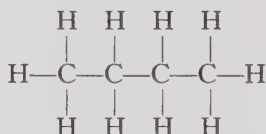


If one of the attached atoms is divalent, this is represented

by drawing two bonds to it, e.g.,



All of the carbon bonds are non-polar in nature, and in general the bond energies are so large that dissociation into ions does not take place. The most important consequence of the non-polar bonds is the formation of long chain carbon molecules, e.g.,



and of complicated compounds of very high molecular weight containing hundreds of atoms. Such compounds constitute plant and animal tissues; from which fact, the term organic chemistry has arisen.

Several types of compounds are formed in which the concept of the four bonds can only be kept by placing two or more of them between adjacent carbon atoms, e.g.,



Such compounds are called "unsaturated." In terms of the "electron pairs" such compounds would be written as

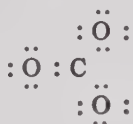


The tetrahedral picture postulates that, in the single bond two tetrahedra are attached by a corner, in the double bond by an edge and in the triple bond by a face. Bond angles have been determined for a number of unsaturated molecules and in most cases, the values are in approximate agreement with the tetrahedral structure.

The electron formulas preserve the idea that carbon always has four bonds, but other electron arrangements must at least be considered as possible, e.g.,



It will be observed that the fundamental difference between saturated and unsaturated carbon compounds is that the latter lack sufficient electrons to complete all of the octets, and there doubtless is resonance between the various electron structures so that no one formula can be written which completely represents the state of the molecule. In carbonates, such as calcium carbonate,  $\text{CaCO}_3$ , the solid is built up of a lattice of calcium and carbonate ions, and the carbonate ion has the three oxygen atoms arranged symmetrically about the carbon in the same plane:



This is a definite example of a compound in which the carbon atom does not have tetrahedral symmetry and the idea of the four bonds can only be preserved by assuming a double bond between one oxygen and the carbon, and in order to give the observed triangular symmetry this double bond must resonate around the molecule.

**3. Occurrence of Carbon.**—Carbon occurs free in the crystalline forms of diamond and graphite. Coal is largely amorphous carbon, although it contains many complex compounds of carbon with hydrogen, as well as with oxygen and nitrogen. Methane,  $\text{CH}_4$ , is the principal constituent of natural gas; and heavier hydrocarbons constitute the mineral oils. The element is found most abundantly in the form of metal carbonates, limestone, or calcium carbonate,

constituting one of the most common minerals. The occurrence of carbon in all animal and plant tissue has been mentioned.

**4. Elementary Carbon.**—Many of the physical properties of **diamond** and **graphite** may be correlated with their crystal structures. The diamond crystal is cubic and each carbon atom is surrounded by four other atoms located at the corners of a regular tetrahedron (Append. V). The four carbon valences are thus satisfied by carbon atoms, and the crystal is held together by bonds which are essentially the same as in the carbon compounds. As a result, diamond is the hardest known substance, and its melting point is probably higher than that of any other element. All of the electrons are doubtless held in the bonds between the atoms, and the crystal is, therefore, a non-conductor of electricity. Diamond has a very high index of refraction, 2.42; and this gives the cut gems a high brilliance, as most of the light falling upon them is totally reflected from the interior surfaces.

Graphite possesses hexagonal symmetry, and crystal structure data indicate planes of carbon atoms in hexagonal rings. Graphite is remarkably soft, and the crystal readily splits off thin flakes. The cleavage planes doubtless are identical with the planes of the carbon atoms of the crystal. Graphite is an elec-

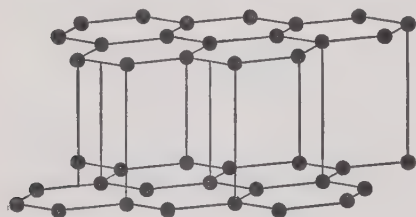


FIG. 1. Crystal structure of graphite.

trical conductor, although only one thousandth as good as copper. This fact is in harmony with the crystal structure in that not all of the carbon bonds are satisfied, and some of the electrons are thus free to move through the crystal.

All forms of carbon are somewhat volatile at  $3500^{\circ}$ , and the vapor, upon condensing, forms graphite. Although the experimental data are somewhat uncertain, the most re-



liable heats of combustion lead to the value:  $C_D = C_G + 220$  cal.; and it may be calculated from this value that diamond at one atmosphere pressure is unstable at all temperatures in respect to graphite. However, diamond is denser than graphite and under 8000 atmospheres at  $25^\circ$  it would become the stable form. Experimentally, it is possible to convert diamond into graphite by heating. Moissan prepared small diamonds by quenching solutions of carbon in molten metals. The contraction of the outer surface of the metal produces great pressure on the interior, thus favoring the formation of the diamond. Naturally occurring diamonds are thought to have been crystallized from solutions of molten magnesium silicates under conditions of great pressure.

The so-called "**amorphous carbon**," such as **charcoal**, appears upon examination by X-rays to resemble graphite in structure, except that it is highly porous or cellular. Upon oxidation by hot nitric acid and potassium chlorate, both charcoal and graphite yield **mellitic acid**,  $C_6(CO_2H)_6$ , a derivative of benzene, thus indicating the ring structure of the carbon in these substances (Par. 16). Charcoal possesses the property of absorbing gas, and, when cooled in liquid air, will absorb air from a sealed tube to produce a vacuum of  $10^{-5}$  mm., or better. Highly active charcoal is used in gas masks for the absorption of poison vapors. The activation is carried out by heating for long periods in steam, which serves to remove adsorbed hydrocarbons from the surface. One cc. of active charcoal is said to have a surface of about 1,000 square meters. Bone charcoal is used in sugar refining to absorb coloring matter present in the crude sugar. Other amorphous forms of carbon are lamp black and carbon black. The former is made by the incomplete combustion of hydrocarbon oils and the latter by impinging the flame of natural gas upon a metal surface. Both are used as pigments in ink, but the carbon black is now far more important. Its largest use is in compounding

rubber for automobile tires. In 1937 over three hundred billion cubic feet of natural gas was consumed in the United States in the production of half a billion pounds of carbon black.

Graphite has long been used for the manufacture of lead pencils. It is obtained from mines in Ceylon and Madagascar, and is now made in large quantities at Niagara Falls by heating anthracite coal in an electric furnace. Because of its infusibility, it is used in making crucibles for use at high temperatures. The presence of a small portion of clay greatly increases its resistance to oxidation. Because of its high melting point, graphite is extensively used for electrodes in electric furnaces. Graphite, or gas carbon, is also used in arc lamp electrodes, cerium fluoride being often added to provide a metal vapor which increases the brilliance of the arc and also reduces its resistance. Ground in oil or water with tannin or other suspending agent, graphite forms a stable suspension, which is used in lubricating bearings. Graphite is also employed extensively in protecting metal surfaces from oxidation, e.g. in stove polish.

Liquid potassium is absorbed by graphite. The alkali atoms apparently enter the crystal between the planes of carbon atoms. Two definite compounds,  $C_8K$  and  $C_{16}K$ , are formed. Powerful oxidizing agents form so-called **graphitic oxide**. Here again the oxygen atoms enter the crystal between the carbon planes. The composition of the product varies from a ratio of oxygen to carbon of 1 to 2.9–3.5. In a similar manner  $HSO_4^-$  groups enter the crystal when graphite is treated with sulfuric acid in the presence of a strong oxidizing agent. The product is known as **blue graphite**, and when treated with water, graphite is again formed. A technical process for the purification of graphite is based on this fact. Fluorine also enters the graphite crystal, forming the explosive **carbon monofluoride**. As in the other absorption reactions the process results in a considerable increase in the volume of the crystal.

TABLE I

## ATOMIC AND PHYSICAL PROPERTIES OF CARBON

Atomic weight.....	12.010	Ionization potential in volts,	
Atomic number.....	6	1st electron.....	11.2
Istopes.....	12, 13	2d electron.....	24.3
Electrons in various quan-		3d electron.....	47.6
tum levels, 1st.....	2	4th electron.....	64.2
2d.....	4	Melting point, ° C.....	G 3500
Density.....	D 3.51	Boiling point, ° C.....	4830
	G 2.25	Electrical resistivity,	
		ohm-cm.....	D $5 \times 10^{14}$
			G $1.4 \times 10^{-3}$

## OXIDES AND ACIDS

5. Carbon forms the monoxide, CO, which is the anhydride of carbonous or formic acid,  $\text{HCO}_2\text{H}$ , and the dioxide,  $\text{CO}_2$ , which is the anhydride of carbonic acid,  $\text{H}_2\text{CO}_3$ . In addition, several anhydrides of more complicated organic acids are known: e.g. carbon suboxide,  $\text{C}_3\text{O}_2$ , the anhydride of malonic acid,  $\text{CH}_2(\text{COOH})_2$ .

TABLE II

## PROPERTIES OF CARBON MONOXIDE AND NITROGEN

	CO	N <sub>2</sub>		CO	N <sub>2</sub>
Melting point.....	- 200°	- 210°	Critical temperature .	- 140°	- 146°
Boiling point.....	- 190°	- 196°	Critical pressure, atm.	36	35
Density of liquid...	0.793	0.796	Critical volume, cc. . .	5.05	5.17

**Carbon monoxide** is remarkably similar to nitrogen in physical properties (Table II). The two gases have the same molecular weight and also the same number (10) of valence electrons. It seems probable from the similarity in properties that the arrangement of the electrons in both molecules may be the same. Probably no single electron structure should be written but rather a number of structures such as,  $:\text{C}:::\text{O}:$  or  $:\text{C}::\ddot{\text{O}}:$  or  $:\text{C}:\ddot{\text{O}}:$  with resonance between them.

Carbon monoxide is but slightly soluble in water, 3 cc. per

100 cc. of water at 8°. It is more soluble in alkalis, giving formates:  $\text{CO} + \text{NaOH} = \text{HCOONa}$ . The gas is readily prepared in the laboratory by the action of sulfuric acid on formic or oxalic acid, or ferrocyanide: (1)  $\text{HCOOH} = \text{CO} + \text{H}_2\text{O}$ , (2)  $\text{H}_2\text{C}_2\text{O}_4 = \text{CO} + \text{CO}_2 + \text{H}_2\text{O}$ , (3)  $\text{K}_4\text{Fe}(\text{CN})_6 + 6\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} = 6\text{CO} + 2\text{K}_2\text{SO}_4 + 3(\text{NH}_4)_2\text{SO}_4 + \text{FeSO}_4$ . The formation from reactions involving carbon, oxygen, and water is discussed in later paragraphs.

Carbon monoxide reacts with many metals, forming **carbonyls**, e.g.,  $\text{Fe}(\text{CO})_5$ ,  $\text{K}_6(\text{CO})_6$ ,  $\text{Ni}(\text{CO})_4$ ,  $\text{Co}_2(\text{CO})_8$ ,  $\text{Cr}(\text{CO})_6$ ,  $\text{W}(\text{CO})_6$ ,  $\text{Ru}(\text{CO})_5$ ,  $\text{Mo}(\text{CO})_6$ . The nickel compound is of especial importance (cf. **XIX—20**). Iron and cobalt form the unusual **carbonyl hydrides**  $\text{Fe}(\text{CO})_4\text{H}_2$  (cf. **XIX—15**) and  $\text{Co}(\text{CO})_4\text{H}$ . The so-called potassium carbonyl appears to be a derivative of hexahydroxy benzene,  $\text{C}_6(\text{OK})_6$ . The oxide enters into a number of "coordination complex ions" such as  $\text{K}_3\text{Fe}(\text{CN})_5\text{CO}$ ; and the gas is absorbed by both acid and ammonical solutions of cuprous chloride with the formation of rather unstable complexes, possibly  $\text{Cu}(\text{CO})\text{Cl}_2^-$ , and  $\text{Cu}(\text{CO})\text{NH}_3^+$ . Such solutions are employed in gas analysis in the estimation of carbon monoxide, although small amounts of the gas are more accurately determined by passing the gas over hot (160°) iodine pentoxide:  $5\text{CO} + \text{I}_2\text{O}_5 = 5\text{CO}_2 + \text{I}_2$ . The iodine is absorbed in iodide solution and titrated with thiosulfate.

Carbon monoxide unites directly with chlorine in the sunlight, or in the presence of active charcoal as a catalyst to form **phosgene**, **carbonyl chloride**,  $\text{COCl}_2$ . The reaction is highly exothermic, and is, therefore, favored by low temperatures (below 350°).

Carbon monoxide is extremely poisonous. Air containing 1 part in 500 will cause unconsciousness in about an hour; and 1 part in 100 will cause death in a few minutes. The physiological action is due to the formation of a bright red compound with the haemoglobin of the blood. Gas masks to protect against carbon monoxide contain a mix-

ture of manganese and copper oxides known as "hopcalite," which acts as a catalyst for the oxidation of the gas to carbon dioxide.

### 6. Equilibria Involving Carbon Monoxide and Dioxide.

—Around  $500^{\circ}\text{C}$ ., carbon (in excess), in an atmosphere of oxygen, gives almost completely carbon dioxide:  $\text{C} + \text{O}_2 = \text{CO}_2$  (1), but at  $1000^{\circ}$ , the reaction (with excess carbon) gives almost pure carbon monoxide:  $2\text{C} + \text{O}_2 = 2\text{CO}$  (2). It follows that in the equilibrium:  $\text{C} + \text{CO}_2 = 2\text{CO}$  (3), high temperature favors the formation of the lower oxide. Data on the equilibrium are given in Table III.

TABLE III  
 $\text{C}(\text{graph}) + \text{CO}_2 = 2\text{CO}$

$t^{\circ}\text{C} \dots \dots$	500	600	800	1000	1200
Per cent $\text{CO}_2$	95	77	7	0.6	0.06

At low temperatures, carbon monoxide is unstable with respect to the decomposition (3) above, but the rate of decomposition is extremely slow; however, around  $300^{\circ}$  platinum or nickel act as efficient catalysts.

With excess oxygen, both carbon and carbon monoxide are oxidized to the dioxide:  $2\text{CO} + \text{O}_2 = 2\text{CO}_2$  (4). Only at extremely high temperatures is reaction (4) reversed and carbon dioxide dissociated (Table IV). The union of carbon monoxide and oxygen is slow at low temperatures, and even at high temperatures, if the gases are perfectly dry. Water, therefore, appears to act as a catalyst.

TABLE IV  
 $\text{CO}_2 = \text{CO} + \frac{1}{2}\text{O}_2$

$t^{\circ}\text{C} \dots \dots \dots$	1122	1550	2000	2600
Per cent $\text{CO}_2$ dissociated	0.01	0.4	2	50

The equilibrium:  $\text{C} + \text{H}_2\text{O}(\text{g}) = \text{CO} + \text{H}_2$  (5) is very important in the manufacture of artificial fuel gas (see

below). At  $25^\circ$ , the equilibrium constant is about  $10^{-16}$ , but at  $600^\circ$  it is about 1; hence there is a rapid change in the direction of the reaction with temperature.

Below  $500^\circ$ , steam will oxidize carbon monoxide:  $\text{CO} + \text{H}_2\text{O}_{(g)} = \text{CO}_2 + \text{H}_2$  (6). This reaction is utilized in the preparation of commercial hydrogen from water gas (Par. 7). Data on the equilibrium are given in Table V.

TABLE V  
 $\text{CO} + \text{H}_2\text{O}_{(g)} = \text{CO}_2 + \text{H}_2$

$t^\circ \text{C} \dots\dots\dots$	400	500	600	800	1000
Per cent CO converted . . . . .	94	86	76	53	38

Reactions between carbon monoxide and hydrogen to form hydrocarbons and alcohols are discussed in Paragraph 37.

The frequent mention of carbon monoxide in metallurgical processes arises through its powerful reducing power, which enables it to remove oxygen from metal oxides: e.g.,  $\text{CuO} + \text{CO} = \text{CO}_2 + \text{Cu}$  (7). The more noble the metal, the greater the tendency for reaction (7) to take place. In certain cases, the reaction is complicated by the formation of carbides.

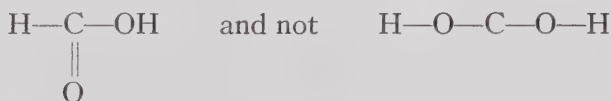
**7. Carbon Monoxide Fuels.**—Carbon monoxide is an important constituent of several artificial fuels. When a limited supply of air is passed through coke or anthracite coal, the resulting mixture is known as **producer gas**, and contains carbon monoxide (30 to 40 per cent), nitrogen (60 per cent), and hydrogen (2 to 5 per cent). A gas of somewhat similar composition, called **blast furnace gas**, is a product of iron smelting. The most important artificial gas, however, is **water gas**, made by passing steam over hot coal. The reaction is endothermic (see reaction (5) above) and in order to maintain the required temperature (around  $600^\circ$ ), it is necessary to turn off the steam every



few minutes and blow air in for a brief period. The resultant mixture of gases consists of carbon monoxide (40 to 50 per cent), hydrogen (45 to 50 per cent), carbon dioxide (3 to 7 per cent), and nitrogen (4 to 5 per cent). In certain localities where crude oil is cheap and coal expensive, **oil-water gas**, for cooking and heating, is made by spraying crude oil and steam upon heated bricks. The heavy hydrocarbons are "cracked" by the heat into carbon and lighter gases, such as  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ ; the former reacts with the steam to form carbon monoxide and hydrogen.

**8. Formic or Carbonous Acid.**—Carbon monoxide reacts with alkalis, producing formates, but does not react with water at ordinary temperatures. However, the equilibrium:  $\text{CO} + \text{H}_2\text{O} = \text{HCO}_2\text{H}$  is attainable at  $150^\circ$  in the presence of hydrogen chloride with the system under pressure; and from measurements of this equilibrium, it may be calculated that formic acid is stable at room temperature with respect to carbon monoxide at one atmosphere. Sulfuric acid readily removes the water from formic acid and evolves carbon monoxide.

Formic acid has the formula,



In this respect, it is similar to the acids of phosphorus. The acid is monobasic, and the dissociation constant is  $1.8 \times 10^{-4}$ . The acid has a pungent, irritating odor, and blisters the skin like a nettle sting. All of the formates are soluble, but the silver and lead salts only moderately.

**9. Carbon Dioxide.**—The product of the oxidation of carbon, free or combined, with excess of oxygen is the dioxide,  $\text{CO}_2$ . This oxide is also formed by the action of acids upon carbonates:  $\text{CaCO}_3 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2$ ; or by the thermal decomposition of carbonates or bicarbonates:  $\text{MgCO}_3 = \text{MgO} + \text{CO}_2$ . An important com-

mercial source of the oxide is the alcoholic fermentation of sugars:  $\text{C}_6\text{H}_{12}\text{O}_6 = 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2$ .

Carbon dioxide occurs in the atmosphere in amounts varying from 3 parts in 10,000 in the country, to 1 part in 100 in crowded and poorly ventilated rooms. It also occurs in effervescent mineral waters, and issues from the ground in large quantities in certain localities, as the Valley of Death, in Java.

Solid carbon dioxide has a vapor pressure of 1 atmosphere at  $-78.5^\circ$ , and therefore sublimates at that temperature.

If heated under pressure, it melts at  $-56^\circ$  (5.3 atm.). The critical temperature of the liquid is  $31.35^\circ$ , the critical pressure, 73 atmospheres. The vapor pressure at  $20^\circ$  is 59 atmospheres. The oxide is usually handled commercially as the liquid in steel cylinders. If the liquid is allowed to flow from the cylinder into a heavy cloth bag, the heat of vaporization is sufficient to cool a

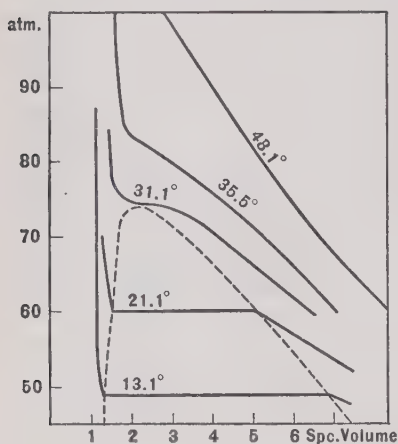


FIG. 2. Pressure-volume curves for  $\text{CO}_2$ .

large fraction of the oxide to the solid state, forming carbon dioxide snow. A solution of the solid in acetone under reduced pressure may be employed to obtain temperatures around  $-110^\circ$ .

The solubility of carbon dioxide in water at 1 atm. pressure and various temperatures is:

$t^\circ \text{C.}$ .....	0	25	40	60
g. $\text{CO}_2$ per 100 g. $\text{H}_2\text{O}$ .....	0.355	0.145	0.097	0.058

Up to about 5 atmospheres, the solubility is nearly proportional to the pressure, following Henry's law, but above that

pressure the solubility becomes greater due to the formation of carbonic acid. Soda water contains carbon dioxide under a pressure of 3 to 4 atmospheres. The rate of the reaction,  $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$  is fairly slow.

The electron structure is generally written as  $:\ddot{\text{O}}::\text{C}::\ddot{\text{O}}:$  but there probably is resonance with other structures, e.g.,  $:\ddot{\text{O}}:\text{C}::\ddot{\text{O}}:$

Carbon dioxide is not poisonous; its harmful effects are due rather to suffocation through lack of oxygen. Air containing 2 to 3 per cent of the gas may be breathed without apparent ill effect, but above 5 per cent panting is produced; and 50 per cent carbon dioxide can be tolerated only for a short time. The high humidity of badly ventilated rooms is probably more harmful than the carbon dioxide content.

The principal use of carbon dioxide is in the preparation of carbonated beverages. Liquid carbon dioxide is used in refrigeration cycles; the solid is used in cold storage, in place of ice, especially in shipping fruit, as the gas liberated tends to prevent the development of aërobic bacteria. The gas is employed in the manufacture of certain carbonates, including the sodium carbonates and white lead. Carbon dioxide is generated in the soda-sulfuric acid type of fire extinguisher. In other types of extinguisher liquid carbon dioxide under pressure is employed. A few per cent of carbon dioxide in air will render it a non-supporter of combustion of most carbonaceous material. A highly electropositive element like magnesium will continue to burn in pure carbon dioxide.

Carbon dioxide is absorbed from the atmosphere by plants, and is the source of the cellulose in plant tissue:  $6\text{CO}_2 + 5\text{H}_2\text{O} = \text{C}_6\text{H}_{10}\text{O}_5 + 6\text{O}_2$ . This reaction (or related reactions) requires the absorption of energy; this is supplied by sunlight through the agency of the chlorophyll. The mechanism of the reaction is much more complicated than

the overall equation indicates. Some carbon dioxide is absorbed in the dark but the regeneration of the active absorbing agent requires light. It is this absorption of radiation by plants, that renders the sun's energy available to us through the use of plants as food, and of plant products, wood, coal, etc., as fuel. The decomposition of plant tissue, of course, returns carbon dioxide to the atmosphere, and this continuous absorption and evolution of carbon dioxide by plants is sometimes referred to as the **carbon cycle**.

**10. Carbonic Acid.**—The structure of carbonic acid has been discussed (Par. 2). The acid is known only in solution, in which it doubtless exists as the meta- rather than the ortho-form. At 1 atmosphere of  $\text{CO}_2$  and  $25^\circ \text{C}$ ., a water solution contains  $0.0338M \text{ H}_2\text{CO}_3$ . The acid is weak, the dissociation constants being, respectively:  $K_1 = 4.3 \times 10^{-7}$ , and  $K_2 = 4.7 \times 10^{-11}$ . A saturated solution (1 atm.) thus contains  $10^{-4}M \text{ H}^+$ . There is considerable evidence that only part of the  $\text{CO}_2$  in a saturated solution is in the form of the acid,  $\text{H}_2\text{CO}_3$ . This would make actual value for  $K_1$  somewhat larger than the value given above.

Due to the weakness of carbonic acid, solutions of the normal carbonates are alkaline from hydrolysis:  $\text{CO}_3^{--} + \text{H}_2\text{O} = \text{HCO}_3^- + \text{OH}^-$ . The concentration of  $\text{OH}^-$  in  $0.5M \text{ Na}_2\text{CO}_3$  is about  $0.01M$ . Bicarbonate ion can either hydrolyze,



or it can ionize further,



The former reaction proceeds farther than the latter, as is shown by the faintly alkaline character of bicarbonate solutions; the concentration of  $\text{OH}^-$  in a molal solution is

about  $2 \times 10^{-6}$ . However, the two reactions tend to assist each other, due to the neutralization of  $H^+$  and  $OH^-$ ; each goes farther than it would in the absence of the other, giving as the result the summation in the reaction,



The equilibrium constant for this very important reaction is  $1.1 \times 10^{-4}$ , corresponding to about  $0.01M$   $CO_3^{--}$  and  $0.01M$   $H_2CO_3$  in  $M$   $NaHCO_3$ . Because of this equilibrium, carbonates are readily converted to bicarbonate by passing carbon dioxide into their solutions; or, if they are but slightly soluble, into a suspension in water. The most important example of such a conversion is the solution of calcium carbonate in excess carbon dioxide:  $CaCO_3 + H_2CO_3 = Ca^{++} + 2HCO_3^-$ . The equilibrium is displaced upon heating by the evolution of carbon dioxide, hence bicarbonates in solution form carbonates upon heating, upon evaporation, or upon neutralization of the carbonic acid. The first of these processes accounts for the formation of scale in kettles and boilers; the second for the formation of stalactites and stalagmites in caves; and the third is used in the softening of water by addition of alkaline reagents, such as ammonia, or by the exactly equivalent amount of calcium hydroxide (cf. V—11).

With the exception of the alkali metals, most of the carbonates are but slightly soluble or else hydrolyze to form basic carbonates or hydroxides. The bicarbonates of the alkali metals are less soluble than the carbonates; those of other metals generally more soluble. Reference should be made to the alkali carbonates for the details of their commercial preparation.

**11. Analysis of Carbonates.**—Carbonates are detected in qualitative analysis by the evolution of carbon dioxide with acids, and the formation of a white precipitate when this is passed into a solution of barium or calcium hydroxide.

When only a trace of carbonate is present, the test is made more delicate by adding a small piece of zinc to the sample, so that the hydrogen evolved will carry the carbon dioxide through the lime water.

The indicator, methyl orange, changes from yellow to red at about  $10^{-4} M H^+$ ; hence, a dilute solution of carbonic acid gives a yellow color; but if a drop of strong acid is added, the color changes to red. Carbonates may, therefore, be titrated with a strong acid, using this indicator. An alternate method is to add an excess of standard acid,

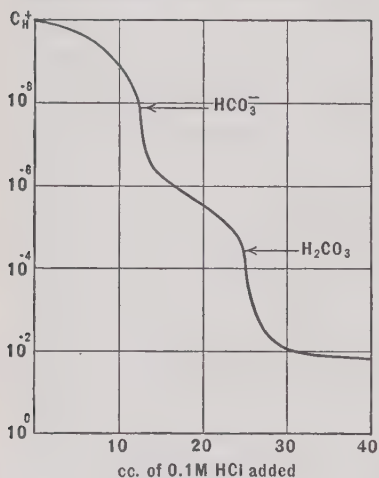


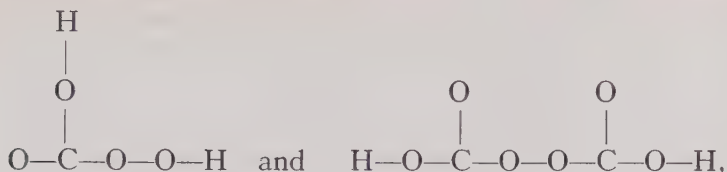
FIG. 3. Titration of carbonate with hydrochloric acid.

remove the carbonic acid by boiling, and titrate the excess of acid with alkali, using phenolphthalein as an indicator. In case hydroxide is present, the carbonate may first be removed by precipitation as barium carbonate. In a mixture of soluble carbonate and bicarbonate, the solution may first be titrated in the cold with a strong acid, using phenolphthalein as an indicator, which gives the amount of

carbonate. To another portion methyl orange is added, and the titration is carried to this end-point. The second step corresponds to the sum of the moles of bicarbonate and twice the moles of carbonate. Or, the analysis may be made (1) by addition of excess of standard base, (2) precipitation of the carbonate by barium ion, (3) filtration of the carbonate and determination of total carbonate by titration, (4) titration of hydroxide in the filtrate to give the amount of bicarbonate by difference.

**12. Peroxycarbonates.**—Salts of the type  $Na_2CO_4$  and  $K_2C_2O_6$  are known, corresponding to the acids





but the free acids are unstable. The monoperoxycarbonates are formed by the interaction of an alkali carbonate and hydrogen peroxide. They may be precipitated from the solution by ether. The salts of the diperoxycarbonic acid may be prepared by the anodic oxidation of solutions of alkali carbonates, cooled to  $-10^{\circ}$  or below. These compounds show the characteristic strong oxidizing power and strong reducing power of other peroxyacids and of hydrogen peroxide. The commercial sodium peroxycarbonate often contains hydrogen peroxide of crystallization, e.g.,  $\text{Na}_2\text{CO}_4 \cdot \text{H}_2\text{O}_2$ .

**13. Carbides.**—Carbon combines directly with many metals at high temperatures to yield carbides. All the main Group I metals form carbides of the general formula,  $\text{M}_2\text{C}_2$ ; and the main Group II (except beryllium),  $\text{MC}_2$ . These compounds and also  $\text{Cu}_2\text{C}_2$  and  $\text{Ag}_2\text{C}_2$  hydrolyze in water with the evolution of acetylene. The rare earth metals form carbides of the same general formula,  $\text{MC}_2$ , but these and other dicarbides, as  $\text{UC}_2$ ,  $\text{ThC}_2$ , and  $\text{MnC}_2$ , hydrolyze to form complex mixtures of solid and liquid hydrocarbons. Beryllium carbide,  $\text{Be}_2\text{C}$ , and aluminum carbide,  $\text{Al}_4\text{C}_3$ , and a number of group four compounds, as  $\text{SiC}$ ,  $\text{TiC}$ , and  $\text{ZrC}$ , hydrolyze to form methane and  $\text{Fe}_3\text{C}$ ,  $\text{Mn}_3\text{C}$ , and  $\text{Ni}_3\text{C}$  yield chiefly methane with some hydrogen. In addition to these so-called salt-like carbides, there exists a number of comparatively non-reacting carbides as  $\text{B}_6\text{C}$ ,  $\text{ZrC}$ ,  $\text{HfC}$ ,  $\text{TaC}$ ,  $\text{Cr}_3\text{C}_2$ ,  $\text{W}_2\text{C}$ ,  $\text{VC}$ ,  $\text{Mo}_2\text{C}$ , and  $\text{MoC}$ . These carbides are high melting and very hard. The mixed carbide  $\text{WTiC}_2$ , known as Kennametal, is used as a hard tool cutting edge. No carbides are formed by

members of the first or the second subgroups, or by tin, lead, arsenic, antimony, or bismuth.

Commercially, the most important carbide is **calcium carbide**. This is made by heating a mixture of lime and carbon in an electric furnace (about  $3000^{\circ}$ ):  $\text{CaO} + 3\text{C} = \text{CaC}_2 + \text{CO}$ . The reaction is highly endothermic. The formation of acetylene and cyanamide from the carbide is discussed under those compounds.

**14. Carbon and Sulfur.**—The **disulfide**,  $\text{CS}_2$ , is formed from sulfur vapor and graphite at very high temperatures, but the equilibrium is reversed at low temperatures. It is, therefore, prepared by heating carbon and sulfur in an electric furnace:  $\text{C} + 2\text{S} = \text{CS}_2$ .

The compound is a heavy, colorless, volatile, highly refractive liquid. It usually has a disagreeable odor from the presence of other sulfur compounds. It has acid properties, and unites with basic sulfides forming thiocarbonate:  $\text{BaS} + \text{CS}_2 = \text{BaCS}_3$ . The liquid is a good solvent. The vapor is highly inflammable and poisonous. It is used in killing rodents, as a solvent for rubber and sulfur, in the preparation of carbon tetrachloride, and in the manufacture of viscose.

The **monosulfide**,  $\text{CS}$ , is prepared by the action of ozone upon carbon disulfide vapor. It may be condensed as a liquid at very low temperatures; upon heating, it polymerizes with explosive violence to a solid.

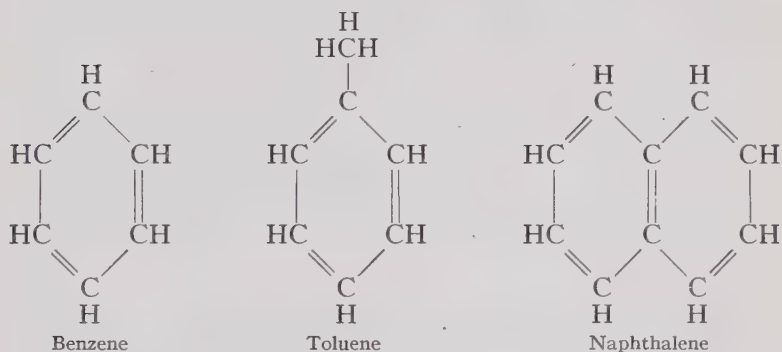
**15. Carbon oxysulfide**,  $\text{COS}$ , forms when carbon disulfide is treated with sulfur trioxide:  $\text{CS}_2 + 3\text{SO}_3 = \text{COS} + 4\text{SO}_2$ . It is a colorless gas, and resembles carbon dioxide in being rather soluble in water.

**16. Carbon and Hydrogen.**—The formation of heavy hydrocarbon molecules has been discussed in the introductory paragraphs of this chapter. These compounds may be considered in two main groups.

(1) The **aliphatic** compounds. The paraffin series, general formula,  $\text{C}_n\text{H}_{(2n+2)}$ , occurs extensively in American

mineral oils. The lighter members of the series,  $\text{CH}_4$  to  $\text{C}_4\text{H}_{10}$ , constitute natural gas. The compounds,  $\text{C}_5\text{H}_{12}$  to  $\text{C}_8\text{H}_{18}$ , constitute the light and heavy gasolines. The members,  $\text{C}_9\text{H}_{20}$  to  $\text{C}_{13}\text{H}_{28}$ , are familiar as lubricating oils, and heavier molecules, up to  $\text{C}_{35}\text{H}_{72}$ , as paraffin wax. Various unsaturated derivatives of the paraffins (Par. 2) may be considered as separate series: such as compounds of the general type,  $\text{C}_n\text{H}_{2n}$ , the olefine series, and  $\text{C}_n\text{H}_{2n-2}$ , acetylene series.

(2) **Aromatic** compounds, consisting of benzene,  $\text{C}_6\text{H}_6$ , and its simple derivatives, such as toluene,  $\text{CH}_3\text{C}_6\text{H}_5$ ; and more complicated double and triple ring compounds, such as naphthalene,  $\text{C}_{10}\text{H}_8$  and anthracene,  $\text{C}_{14}\text{H}_{10}$ .



These hydrocarbons occur in certain types of mineral oils and in the liquid, condensate from the destructive distillation of coal.

**17. Methane**,  $\text{CH}_4$ , has been mentioned as the principal constituent of natural gas. It was formerly known as marsh gas, and was first observed as bubbles rising from the decomposition of vegetable matter in swamps. The gas has a low freezing and boiling point, and is but slightly soluble in water (5.5 cc. per 100 cc. of water at  $0^\circ$ ).

The gas may be formed by the direct reaction of carbon and hydrogen, at moderately high temperatures, Table VI.

TABLE VI  
EQUILIBRIUM VALUES FOR THE REACTION,  
 $C + 2H_2 = CH_4 + 183,000 \text{ cal.}$

$t^\circ \text{C.}$ .....	400	600	800	1000	1200
Per cent $CH_4$ .....	86	32	4	1	0.2

The reaction is obviously favored by high pressure.

Methane is also formed by the reaction of carbon monoxide and hydrogen:  $CO + 3H_2 = CH_4 + H_2O$ , at low temperatures,  $250\text{--}300^\circ$ , in the presence of certain catalysts (Par. 37). At high temperatures, the equilibrium is reversed.

The laboratory preparation of methane is usually carried out by heating a mixture of sodium acetate and soda lime, or by the action of water on aluminum carbide:  $CH_3COONa + NaOH = Na_2CO_3 + CH_4$ , and  $Al_4C_3 + 12H_2O = 3CH_4 + 4Al(OH)_3$ .

**18. Acetylene**,  $C_2H_2$ , is formed in small amounts by the reaction of carbon and hydrogen at very high temperatures ( $2500^\circ$ ):  $2C + H_2 = C_2H_2$ . It is prepared commercially by the action of water on calcium carbide:  $CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2$ .

The gas is colorless and odorless when pure, but usually has a pungent odor due to the presence of traces of phosphine. The vapor pressure of the liquid is about 40 atmospheres at  $20^\circ$ ; and under these conditions it is highly explosive, as at ordinary temperatures the gas is unstable in respect to hydrogen and carbon. It is usually handled as a solution in acetone under pressure in steel cylinders.

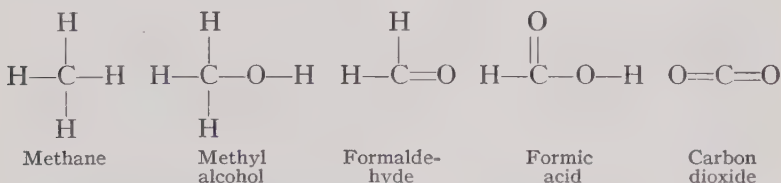
The temperature of the oxy-acetylene torch,  $2500$  to  $3000^\circ \text{C.}$ , is hotter than that of any other flame, with the possible exception of that of atomic hydrogen (cf. I—9); and this is employed extensively in cutting and welding steel and other metals. Before the introduction of the incandescent electric globe, the acetylene lamp was of considerable importance.

Acetylene acts as a very weak acid. Silver acetylide,  $\text{Ag}_2\text{C}_2$ , is formed by passing the gas through a solution of silver ammonia hydroxide. Many of the acetylides are explosive.

At high temperatures acetylene polymerizes to a number of complex products, among them being benzene,  $3\text{C}_2\text{H}_2 = \text{C}_6\text{H}_6$ . As an unsaturated compound, it readily adds hydrogen or halogens to form, respectively, ethane or its halogen derivatives of the type  $\text{C}_2\text{H}_2\text{X}_4$ .

The condensation of acetylene also yields derivatives of the **vinyl** group,  $\text{CH}_2=\text{CR}^-$ . Thus vinyl acetate,  $\text{CH}_3\text{COOCH}=\text{CH}_2$  is made by the condensation with acetic acid, using mercuric oxide and sulfur trioxide as a catalyst. This and similar derivatives form the basis for the rapidly developing vinyl plastic industry. In the presence of mercurous sulfate acetylene adds water to form acetaldehyde,  $\text{CH}_3\text{CHO}$ . This may be reduced to ethyl alcohol or oxidized to acetic acid. These also are important commercial syntheses.

**19. Oxidation Products of the Hydrocarbons.**—The oxidation of methane leads to the following series of oxidation products:



The half reactions involved in these oxidations and their approximate potentials in water solutions are the following:

	VOLTS <sub>25°</sub>
$\text{CH}_4 + \text{H}_2\text{O} = \text{CH}_3\text{OH} + 2\text{H}^+ + 2e^-$ .....	- 0.58
$\text{CH}_3\text{OH} = \text{HCHO} + 2\text{H}^+ + 2e^-$ .....	- 0.24
$\text{HCHO} + \text{H}_2\text{O} = \text{HCOOH} + 2\text{H}^+ + 2e^-$ .....	0.01
$\text{HCOOH} = \text{CO}_2 + 2\text{H}^+ + 2e^-$ .....	0.14

Related compounds result from the oxidation of other hydrocarbons; and these compounds are generally classified

on the basis of the following characteristic groups, where R represents an organic radical formed by the removal of one hydrogen ion from a hydrocarbon, e.g. ethyl,  $C_2H_5$ , from ethane,  $C_2H_6$ .

$R-OH$	Alcohols—organic bases	$\begin{array}{c} H \\   \\ R-C=O \end{array}$	Aldehydes
$\begin{array}{c} O \\    \\ R-C-R \end{array}$	Ketones	$\begin{array}{c} O \\    \\ RC-OH \end{array}$	Acids
$R-O-R$	Ethers—by removing water from two alcohol molecules		
$\begin{array}{c} O \\    \\ RC-OR \end{array}$	Esters—“salts” of an alcohol and organic acid.		

**20. Carbohydrates.**—An important class of organic compounds contains hydrogen and oxygen in the same proportion as in water, and are termed carbohydrates. The group includes **cellulose**,  $(C_6H_{10}O_5)_x$ , starch,  $(C_6H_{10}O_5)_x$ , and the sugars. The latter are generally classified as **monosaccharides**,  $C_6H_{12}O_6$ , such as **glucose** or **fructose**; and as **disaccharides**,  $C_{12}H_{22}O_{11}$ , such as **sucrose** (cane sugar), or **lactose** (milk sugar). These compounds are really alcohol, and aldehyde or ketone derivatives of long chain hydrocarbons, e.g., glucose is  $CH_2OH \cdot CHO \cdot CHO \cdot CHO \cdot CHO \cdot CHO$ .

The molecular weights of cellulose and starch are not known, but the molecules are very complex. Starch may be converted to glucose by boiling in a solution containing a little hydrochloric acid:  $(C_6H_{10}O_5)_x + xH_2O = xC_6H_{12}O_6$ . Under similar conditions, sucrose may be hydrolyzed to a mixture of glucose and fructose.

**21. Halogens and Hydrocarbons.**—Any hydrogen in a hydrocarbon is capable of being replaced by a halogen atom, thus making possible thousands of halogen hydrocarbon



derivatives. The replacement can often be accomplished by direct action of the halogen as a gas, or in alkaline solution upon the hydrocarbon, e.g.  $C_2H_6 + Cl_2 = C_2H_5Cl + HCl$ . Reactions between alcohols and halogen acids may also be employed:  $C_2H_5OH + HCl = C_2H_5Cl + H_2O$ . A few of the more important compounds are discussed below.

**Carbon tetrachloride**,  $CCl_4$ , is made by passing a mixture of carbon disulfide vapor and chlorine through a red hot tube:  $CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2$ . The tetrachloride may be separated by fractional distillation from the sulfur chloride. Or, the reaction may be carried out by passing chlorine gas through the disulfide in the presence of a small amount of iodine. Carbon tetrachloride is a heavy, colorless liquid. It is non-inflammable, and a good solvent for non-polar substances; whence its use in dry cleaning, and in fire extinguishers, e.g. "pyrene." The vapors are slightly toxic.

**Chloroform**,  $CHCl_3$ , is prepared by the action of bleaching powder on alcohol. It is a heavy liquid, and is used largely as an anaesthetic.

**Iodoform**,  $CHI_3$ , is prepared by the action of iodine in alkaline solution on alcohol. It is a solid with a pungent characteristic odor, and finds extensive use as an antiseptic.

**Ethyl chloride**,  $C_2H_5Cl$ , is formed when ethane is treated with chlorine in the sunlight, or alcohol is treated with phosphorus pentachloride. It is a volatile liquid which is employed in refrigerant cycles, and as a local anaesthetic.

**Ethylene dichloride**,  $C_2H_4Cl_2$ , is used in the manufacture of the polysulfide rubbers such as **Thiokol**, through its reaction with polysulfide. The product,  $C_2H_4S_2$ , polymerizes in the presence of zinc oxide to a plastic. The dichlorodifluoromethane,  $CCl_2F_2$ , called **Freon**, has become important as a non-inflammable readily condensable gas for refrigeration cycles. Cf. also CF, Par. 4.

**22. Carbon and Nitrogen.**—The nitride,  $C_2N_2$ , **cyanogen**, may be considered as the polymerized free cyanide radical,

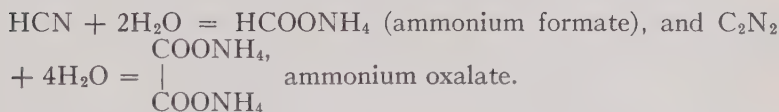
since it is formed by the oxidation of cyanides. The chemistry of the cyanides resembles in many respects that of the halogens, especially iodine; and the methods of preparation of cyanogen, by heating the compounds of the noble metals, and by the reaction with cupric ion, are analogous to the liberation of iodine under these conditions:  $2\text{AuCN} = 2\text{Au} + \text{C}_2\text{N}_2$ ,  $\text{Hg}(\text{CN})_2 = \text{Hg} + \text{C}_2\text{N}_2$ ,  $2\text{Cu}^{++} + 4\text{CN}^- = 2\text{CuCN} + \text{C}_2\text{N}_2$ . The reaction,  $\text{C}_2\text{N}_2 = 2\text{C} + \text{N}_2$ , is highly exothermic (about 80,000 cal.). Many references are made in the chemical literature to the formation of cyanogen in the electric arc, but it is doubtful if, even at that high temperature, an appreciable quantity of the compound can be formed by direct union of the elements.

Cyanogen is a colorless gas, has a distinctive odor, and is extremely poisonous. It is soluble in water (4 volumes per 1 volume of water at  $0^\circ$ ). When heated to  $400^\circ$  the gas polymerizes to a white solid, **paracyanogen**,  $(\text{CN})_x$ . In alkaline solution, cyanogen hydrolyzes to cyanide and cyanate:  $\text{C}_2\text{N}_2 + 2\text{OH}^- = \text{CN}^- + \text{CNO}^- + \text{H}_2\text{O}$  (compare  $\text{Cl}_2 + 2\text{OH}^- = \text{Cl}^- + \text{ClO}^- + \text{H}_2\text{O}$ ). In sunlight, it decomposes, forming ammonium oxalate, ammonium formate, and urea. The potentials for the oxidation and reduction of  $\text{C}_2\text{N}_2$  in acid solution are:  $\text{H}_2\text{O} + \frac{1}{2}\text{C}_2\text{N}_2 = \text{HCNO} + \text{H}^+ + e^-$ , 0.27 volt and  $\text{HCN} = \frac{1}{2}\text{C}_2\text{N}_2 + \text{H}^+ + e^-$ , - 0.33 volt.

**23. Hydrogen Cyanide**, or "prussic acid," may be prepared by the action of dilute sulfuric acid upon an alkaline cyanide, as it is a weak volatile acid. With concentrated sulfuric acid, carbon monoxide is evolved:  $\text{HCN} + \text{H}_2\text{O} + \text{H}^+ = \text{CO} + \text{NH}_4^+$ . The acid is also liberated by the dehydrating action of phosphorus pentoxide upon ammonium formate:  $\text{HCOONH}_4 = \text{HCN} + 2\text{H}_2\text{O}$ . Compounds of hydrogen cyanide with sugars (glucosides) occur in nature, e.g. in leaves and seeds of the peach tree; a solution made by boiling peach leaves in water was used by the ancient Egyptians as a poison.

Liquid hydrogen cyanide boils at  $26.5^{\circ}$ . The gas has the odor of bitter almonds, and is extremely poisonous. It is readily soluble in water, like the halogen acids; but unlike them it is a weak acid,  $K_{18}^{\circ} = 4 \times 10^{-10}$ . With chlorine in solution **cyanogen chloride** is formed:  $\text{HCN} + \text{Cl}_2 = \text{HCl} + \text{CNCl}$ . Alkaline oxidizing agents oxidize cyanide to cyanate (see below), while acid oxidizing agents usually yield carbon dioxide and ammonia.

The arrangement of the 10 electrons in cyanide ion may be  $:\text{C}::\ddot{\text{N}}:$  or  $:\text{C}:::\text{N}:$  or probably both with resonance between the structures. When the bond between the carbon and nitrogen is broken by hydrolysis, however, 8 of the 10 electrons go with the nitrogen, forming ammonium: thus,



**24. The Alkali Cyanides** are important commercial compounds (cf. IV—21). They may be prepared: (1) from alkali ferrocyanide by fusion with sodium metal:  $\text{K}_4\text{Fe}(\text{CN})_6 + 2\text{Na} = 4\text{KCN} + 2\text{NaCN} + \text{Fe}$ ; (2) by heating the ferrocyanide with carbonate:  $\text{K}_4\text{Fe}(\text{CN})_6 + \text{K}_2\text{CO}_3 = 5\text{KCN} + \text{KOCN} + \text{CO}_2 + \text{Fe}$ ; (3) by the reactions:  $2\text{NH}_3 + 2\text{Na} = 2\text{NH}_2\text{Na} + \text{H}_2$  ( $300\text{--}400^{\circ}\text{C.}$ ) and  $2\text{NaNH}_2 + 2\text{C} = 2\text{H}_2 + 2\text{NaCN}$  (red heat); (4) from calcium cyanamide by fusion with sodium carbonate:  $\text{CaCN}_2 + \text{C} + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{NaCN}$ ; (5) by the Bucher process for the fixation of nitrogen, by heating a mixture of sodium carbonate, carbon, and iron (catalyst) made into bricks in an atmosphere of nitrogen:  $\text{Na}_2\text{CO}_3 + 4\text{C} + \text{N}_2 = 2\text{NaCN} + 3\text{CO}$ . The cyanide is extracted with liquid ammonia.

The alkali cyanides are readily soluble in water, and the solutions are alkaline by hydrolysis. Many complex cy-

anides are remarkably stable. Ions of the type  $M(CN)_4^{-4+n}$  are formed by  $Cu^+$ ,  $Cd^{++}$ ,  $Ni^{++}$ ,  $Hg^{++}$ ,  $Pd^{++}$ , and  $Pt^{++}$ ; of the type  $M(CN)_6^{-6+n}$  by  $Cr^{++}$ ,  $Cr^{+++}$ ,  $Co^{++}$ ,  $Co^{+++}$ ,  $Fe^{++}$ ,  $Fe^{+++}$ ,  $Mn^+$ ,  $Mn^{++}$ ,  $Mn^{+++}$ ,  $Rh^{+++}$ ,  $Ru^{++}$ ,  $Os^{++}$ ,  $Ir^{+++}$ ,  $V^{+++}$ ,  $V^{+4}$ , and  $W^{+4}$ . A few complex cyanides of the type  $M(CN)_3^{-3+n}$  are known, e.g.,  $Cu^+$ ,  $Ni^+$ ,  $Mn^{++}$ , but they usually readily add another group. Silver forms the ion  $Ag(CN)_2^-$ .

**25. Cyanates** are readily prepared by the action of mild oxidizing agents upon cyanides, for example, by heating potassium cyanide with lead oxide:  $KCN + PbO = KOCN + Pb$ . The salt is extracted from the lead with alcohol, as the water solution is unstable:  $KOCN + 2H_2O = NH_3 + KHCO_3$ . Cyanate is also formed by the action of cyanide upon copper ammonia ion:  $2Cu(NH_3)_4^{++} + 3CN^- + 2OH^- = 2CuCN + OCN^- + 8NH_3 + H_2O$ . The cyanide-cyanate potential



The free acid decomposes very readily into carbon dioxide and ammonia in water solution. **Ammonium cyanate**,  $NH_4OCN$ , is isomeric with **urea**:  $NH_4OCN = CO(NH_2)_2$ . The rearrangement takes place upon evaporating an aqueous solution.

**26. Thiocyanates** may be prepared by fusing alkali cyanides with sulfur:  $KCN + S = KSCN$ . The ammonium salt is formed by the reaction of ammonia and carbon disulfide:  $4NH_3 + CS_2 = NH_4SCN + (NH_4)_2S$ . At  $140^\circ$ , this salt rearranges to **thiourea**,  $CS(NH_2)_2$ . The free acid,  $HSCN$ , is a liquid which readily polymerizes to a yellow solid.

**27. Calcium Cyanamide** is important in its relation to the cyanamide process for the fixation of nitrogen. Around  $1000^\circ$ , calcium carbide absorbs nitrogen to form cyanamide:  $CaC_2 + N_2 = CaCN_2 + C$ . The product is used directly as a fertilizer, or treated with superheated steam to convert

the nitrogen into ammonia:  $\text{CaCN}_2 + 3\text{H}_2\text{O} = \text{CaCO}_3 + 2\text{NH}_3$ . At low temperatures, the hydrolysis product is cyanogenamide:  $2\text{CaCN}_2 + 4\text{H}_2\text{O} = 2\text{Ca}(\text{OH})_2 + (\text{CNNH}_2)_2$ . The world's production of cyanamide in 1938 was about a million tons. The preparation of cyanide from cyanamide has been mentioned above.

**28. The Proteins** constitute a class of extremely complicated nitrogen compounds, occurring in animal and vegetable tissue. Empirical formulas, calculated from the percentage composition, give results such as  $\text{C}_{146}\text{H}_{226}\text{N}_{44}\text{SO}_{50}$ , but the molecular weights appear to be much higher. The proteins are complexes of amino-acids, i.e. compounds con-

taining the groups  $\text{NH}_2\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}-$  and  $-\text{COOH}$ , such as glycine,  $\text{CH}_2\text{NH}_2\text{COOH}$ .

## THE ORGANIC CHEMICAL INDUSTRIES

Many references have been made to the use of inorganic chemicals in various organic industries. For the sake of clarifying these references, brief outlines of some of the more important industries will be given.

**29. Explosives.**—One of the most important explosives is **nitroglycerine** (cf. also **XII—36**). This compound is very easily detonated by shock:  $4\text{C}_3\text{H}_5(\text{NO}_3)_3 = 12\text{CO}_2 + 10\text{H}_2\text{O} + 6\text{N}_2 + \text{O}_2$ . Like all good explosives, the heat of the reaction is large, and the gaseous products tend to occupy a very large volume in comparison to the original compound. **Dynamite** was formerly made by absorbing nitroglycerine in a porous earth; this form is now generally replaced by solutions of guncotton in nitroglycerine, known as **blasting gelatine**, giant powder, etc. Diethylglycol dinitrate,  $\text{C}_2\text{H}_4(\text{NO}_3)_2$ , is now being used somewhat in place of nitroglycerine. **Guncotton**, or cellulose trinitrate,  $\text{C}_6\text{H}_7\text{O}_2(\text{NO}_3)_3$ , is formed by steeping cotton in a cold mixture of nitric and sulfuric acids. It explodes when detonated



by another explosive. **Smokeless powder**, or **cordite**, is made by evaporating a solution, in acetone, of guncotton, nitroglycerine, and a little vaseline.

The high explosives employed in shells to produce violent shattering are **trinitrotoluene**, "TNT,"  $\text{CH}_3\text{C}_6\text{H}_2(\text{NO}_2)_3$ , and **picric acid**,  $\text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)_3$ . A mixture of the former with ammonium nitrate is known as **amatol**.

**30. Cellulose.**—The extraction of pure cellulose from the mineral and ligneous matter of wood and other plant fibers (especially cotton) has become one of the most important chemical industries. The wood or plant fibers are ground with water to give a mechanical pulp. Three types of chemical pulp, consisting of more or less pure cellulose are in use in America: (1) **soda pulp**, made by heating the mechanical pulp with 10 per cent NaOH under pressure, (2) **sulfite pulp**, made by digestion with a solution of calcium bisulfite and free sulfurous acid, (3) **sulfate pulp** made by treatment with sodium sulfate solution which contains some NaOH and  $\text{Na}_2\text{S}$ . Large quantities of chlorine are also employed in the bleaching of these pulps. In Europe wheat and flax straw are treated by the Pomelio process which employs chlorine gas in dilute sodium hydroxide to dissolve out the non-cellulose constituents. There are three forms of cellulose,  $\alpha$ ,  $\beta$ , and  $\gamma$ . The alpha form is insoluble in 18 per cent NaOH at  $20^\circ\text{C}$ . and is the most desirable. Cotton linters give a pulp which is 98 per cent alpha cellulose.

**Paper** is made from various mixtures of mechanical and chemical pulp, the proportion depending upon the type and grades.

For the synthetic textile and plastic industries the cellulose is dissolved by one of the following methods: (1) the cellulose is treated with  $\text{CS}_2$  and NaOH to form a xanthate solution (**viscose** process). The cellulose is reprecipitated by acid. (2) The cellulose is nitrated and the nitrocellulose dissolved in suitable solvents. (3) The solvent is ammoniacal copper solution. The cellulose is coagulated in a caustic



bath. (4) Cellulose acetate is made by dissolving the pulp in a mixture of acetic anhydride and glacial acetic acid. Cellulose acetate may be precipitated by water. The process is modified to give other esters in addition to the acetate and also cellulose ethers.

**31. Rayon and other Textiles.**—Any of the cellulose solutions discussed above may be employed to form threads. The liquid is forced through a small opening and coagulated. The resulting thread is gathered, washed, and wound. The 1937 production of American rayon was 343,000,000 pounds. About 70 per cent of this was produced by the viscose process and practically none from nitrocellulose although this was the first of the artificial silks. The new **nylon** is not a cellulose but is a polymide and thus more nearly like natural silk in composition. The most promising artificial wool fabric is the casein fiber, **lanitol** being an example. The casein is dissolved in sodium hydroxide and the solution extruded into an acid formaldehyde bath to precipitate it. Casein is a protein substance as is wool, and the fiber has many of the properties of natural wool.

**32. Plastics.**—One of the earliest plastics was celluloid which was made by combining nitrocellulose with camphor and castor oil. Dissolved in alcohol and ether, the nitrocellulose formed a lacquer known as **collodion**. The name **Pyroxylin** is now given to this class of plastics and lacquers. The plasticizing agent camphor has now been supplemented by many others such as the organic phosphates, and derivatives of phthalic acid. All of the cellulose solutions (Par. 30) may be made into plastics. One of the most extensive uses of cellulose acetate is as laminating material for safety glass. In 1938 about twenty-five million pounds of **cellophane** was produced from viscose for use as a wrapping material.

Another type of plastics is the artificial ambers, as, for example, **Bakelite**, formed by the condensation of phenol,  $C_6H_5OH$ , with formaldehyde,  $CH_2O$ , or with other alde-

hydes, as furfural,  $C_5H_4O_2$ . The vinyl resins (cf. Par. 18) are also used in safety glass and are employed as the material for many molded articles. **Acrylate resins** are esters of methacrylic acid,  $CH_2=C(CH_3)-COO-R$ . They give crystal clear glass like molds. The plastic **lucite** belongs to this class. **Urea-formaldehyde** resins are also glass-like. Casein, soy bean protein, and lignin are examples of waste materials which are now employed in plastics. The casein is made into a dough with filler and coloring matter, pressed into shape and set by treatment with formaldehyde solution. It is used chiefly in the manufacture of buttons.

**33. Rubber.**—The raw rubber as it comes from the plantation is a soft somewhat sticky substance which probably consists of long chains of polymerized molecules having the general formula,  $C_5H_8$ . At the factory it is softened with steam and mixed with the compounding agents (principally carbon black and zinc oxide) and with the vulcanizer, sulfur. Vulcanization requires heating to a temperature of 120 to 200° and doubtless results in the formation of cross linkage between the long carbon chains through the action of the

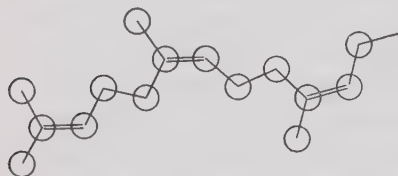


FIG. 4. Diagrammatic representation of chains of  $C_5H_8$  molecules in rubber.

sulfur atoms on the unsaturated molecules. Vulcanization decreases the plasticity and increases the resistance to abrasion.

Small objects are often vulcanized by the vapor cure, using sulfur chloride. Recent developments have been the introduction of "accelerators" such as hexamethylenetetraamine,  $(CH_2)_6N_4$ , which lower the temperature and the time required for vulcanization and of "anti-oxidants" which retard the appearance of brittleness due to atmospheric oxidation.

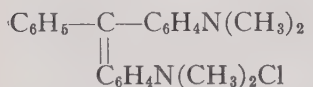
The artificial polysulfide rubber, thiokol, has been discussed in Par. 21. Another synthetic rubber, **neoprene**, is made from monovinyl acetylene (cf. Par. 18). This sub-

stance reacts with hydrogen chloride to give chloroprene which can be polymerized to neoprene.

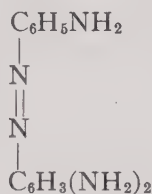
**34. Petroleum.**—Crude oil varies greatly in composition. Some oils (the Pennsylvania) contain largely members of the paraffin series, while others (the California) consist of aromatic groups with varieties of side chains. The properties of light and heavy constituents also vary from one field to another. By distillation the crude oil is separated into (a) volatile gases, (b) gasoline, (c) solvent naphtha, (d) kerosene, (e) lubricating oil, (f) wax tar and fuel oil. The various products are agitated with sulfuric acid, and washed with water and dilute caustic soda. If the crude is high in sulfur an agitation with a solution of lead oxide in sodium hydroxide may also be used. Since the greatest demand has been for gasoline, the higher-boiling constituents are heated to a high temperature ("cracking") to cause their decomposition into lighter hydrocarbons. However, the older methods are being displaced by more efficient processes. One of these is the catalytic hydrogenation of both the heavy fractions and also of the gas oil. This tends to remove oxygen, nitrogen, and sulfur as their hydrogen compounds, to remove the unsaturated molecules which tend to condense to form gums and to give superior lubricating oils and gasolines. Another recent development has been the polymerization of the more volatile constituents, especially propane and butane. The hydrocarbons are generally cracked at relatively low temperature, cooled, and catalytically polymerized. The solvent extraction method by which a lubricating oil may be resolved into a desirable paraffinic oil and a less desirable, less heat resistant fraction by the use of selective solvents such as phenol and dichloroethyl ethers is now in general use. Modern refining methods endeavor to promote the formation of branch chain hydrocarbons, such as isooctane, which have high "anti-knock" qualities. The use of lead tetraethyl,  $\text{Pb}(\text{C}_2\text{H}_5)_4$ , as an "anti-knock" has also become universal.

The production of gasoline in the United States in 1936 was 230 million bbls. straight run from crude and 240 million bbls. from cracking operations.

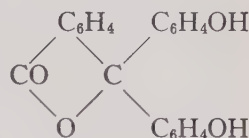
**35. Dyes, Perfumes, and Drugs.**—Compounds of aromatic hydrocarbons constitute almost 100 per cent of textile dyes. Many of these compounds are synthesized from aniline,  $C_6H_5NH_2$ , obtained from the distillation of coal tar. Examples of important types of color compounds are given below:



Malachite green

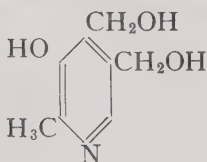
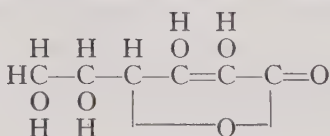


Bismarck brown

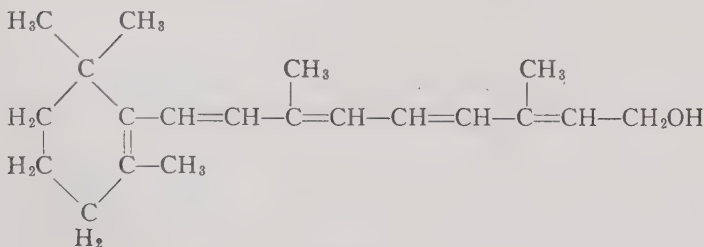


Phenolphthalein

The flavors and perfumes are largely esters and aldehydes, such as "banana oil," amylacetate,  $CH_3COOC_5H_{11}$ . The organic drugs embrace a large number of different types of compounds. The **alkaloids**, as morphine and strychnine, are complex nitrogen compounds. **Aspirin**,  $C_6H_4OAc \cdot COOH$ , is a derivative of salycilic acid. **Salvar-**

Vitamin B<sub>6</sub>

Vitamin C

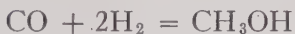
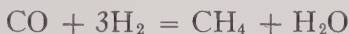


Vitamin A

**san**, used in the treatment of syphilis, is  $\text{NH}_2\text{OHC}_6\text{H}_3\text{As}-\text{AsC}_6\text{H}_3\text{OHNH}_2$ . The isolation, identification, and synthesis of many of the vitamins has now made these substances available as pure chemicals. Examples are given on page 292.

**36. War Gases.**—Chlorine, and soon after, phosgene,  $\text{COCl}_2$ , were employed in the World War in the earlier operations of the gas warfare; later a number of organic derivatives were used, among which were "mustard gas,"  $(\text{CH}_2\text{ClCH}_2)_2\text{S}$ ; chlorpicrin,  $\text{CCl}_3\text{NO}_2$ ; "tear gas," such as brombenzyl cyanide,  $\text{C}_6\text{H}_5\text{CHBrCN}$ ; and "sneeze gas," diphenylchlorarsine,  $(\text{C}_6\text{H}_5)_2\text{AsCl}$ .

**37. Synthetic Methanol.**—In the presence of catalysts, carbon monoxide and hydrogen will combine to form a number of hydrocarbons and alcohols, or other oxidation products of hydrocarbons, for example,



Of these reactions, the most important commercially is the formation of methyl alcohol,  $\text{CH}_3\text{OH}$ , or **methanol**. The reaction is favored by pressure (100–200 atmospheres are used), and the temperature range is between 300 and 600° C. Various mixed metal oxides are employed as catalysts. Zinc oxide favors the formation of methanol, while cobalt metal with chromium oxide yields hydrocarbons. Methanol is important as a solvent, and as a raw material for the synthesis of many organic compounds. It is a very satisfactory fuel for gas engines.

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## Chapter XIV

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### SILICON

1. Silicon, the second element of Group IV, occupies as important a position in the mineral world as carbon does in the vegetable and animal. Its chemistry is characterized by the stability and complexity of the compounds of the dioxide,  $\text{SiO}_2$ , with basic oxides. In this respect, it resembles boron more closely than it does carbon. Although it forms hydrogen compounds similar to those of carbon, the bond between the silicons is readily broken, and the compounds do not possess the stability or importance of the corresponding carbon compounds. The oxide like that of boron is high melting and non-volatile, and many of its compounds are derivatives of polyacids, which resemble the boric acids. However, the majority of the silicates are salts of ortho or meta silicic acid, and thus contain the groups  $\text{SiO}_4$  and  $\text{SiO}_3$ , the former having a charge of  $+4$  and the latter of  $+2$ . Although a monoxide is known, few  $+2$  or unsaturated compounds have been prepared.

In connection with the resemblance between boron and silicon, reference should be made (cf. III—7) to the similarity in the values for the field of force about  $\text{B}^{+3}$  and  $\text{Si}^{+4}$ .

2. **Occurrence.**—Silicon is never found as the free element. The dioxide and its compounds constitute about 87 per cent of the earth's crust, and the element is estimated as forming 25.8 per cent of the outer portions of the earth. Silicon thus ranks next to oxygen in abundance. The principal silicon minerals are summarized in Table VI, and the



important groups, such as the feldspars, pyroxenes, amphiboles, and micas, are discussed in subsequent paragraphs.

**3. Elementary Silicon** has been prepared in a semi-metallic crystalline form, and also in a so-called amorphous form. The former possesses a grey luster and fair electrical conductivity (Table I). Both forms appear, from X-ray data, to have the same atomic arrangement in the crystal, the modified diamond type, hence the amorphous form is probably a mass of very small crystals.

Amorphous silicon is prepared by the high temperature reduction of silicon halides by alkali metals, or of the dioxide by magnesium:  $\text{SiCl}_4 + 4\text{Na} = \text{Si} + 4\text{NaCl}$ . When the dioxide, or sodium silico-fluoride,  $\text{Na}_2\text{SiF}_6$ , is reduced with excess of aluminum, the silicon dissolves in the excess metal, and upon cooling, separates in the crystalline metallic form. This may be separated from the aluminum by dissolving the latter in acid. The metallic form may also be prepared by the reduction of the dioxide with carbon in an electric furnace, although it is difficult to avoid the formation of the carbide. Amorphous silicon may be converted to the metallic form by recrystallizing from molten silver.

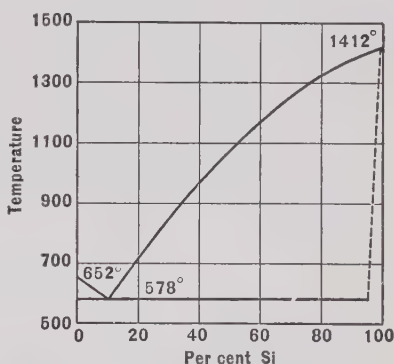


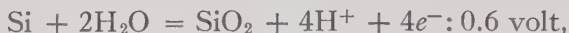
FIG. 1. Aluminum-silicon diagram.

TABLE I  
ATOMIC AND PHYSICAL PROPERTIES OF SILICON

Atomic number.....	14	Density (crys.).....	2.4
Atomic weight.....	28.06	Melting point, ° C.....	1427
Isotopes.....	28, 29, 30	Boiling point, ° C.....	2287
Electrons in various quantum levels, 1st.....	2	Electrical resistivity, ohm-cm.....	$85 \times 10^{-8}$
2d.....	8	Radius of $\text{Si}^{+4}$ in crystals, cm, $\times 10^8$ .....	0.41
3d.....	4		

Silicon is of considerable importance in the steel industry. It is generally prepared, however, as ferrosilicon (Par. 6).

**4. Reactions of the Element.**—Silicon burns in oxygen, but not readily, as a surface layer of oxide tends to stop the reaction. It ignites spontaneously in fluorine at room temperature, in chlorine at 300–350°, in bromine at 500°; and the amorphous form reacts with iodine at red heat, but without luminosity. The oxidation reduction potential,



is not of great significance because of the slowness of the reaction. Thus, silicon is not soluble in hydrogen ion, but due to the great stability of silicates, it does dissolve in sodium hydroxide with the evolution of hydrogen. The element is also oxidized by steam. A mixture of nitric and hydrofluoric acid gives silicon tetrafluoride. Combination occurs with nitrogen and sulfur at high temperature, and with many metals to form silicides.

TABLE II  
REACTIONS OF SILICON

$\text{Si} + \text{O}_2 = \text{SiO}_2$	Not rapid
$\text{Si} + 2\text{X}_2 = \text{SiX}_4$	With halogens
$\text{Si} + 2\text{NaOH} + \text{H}_2\text{O} = \text{Na}_2\text{SiO}_3 + 2\text{H}_2$	
$\text{Si} + 2\text{H}_2\text{O} = \text{SiO}_2 + 2\text{H}_2$	With steam
$3\text{Si} + 4\text{HNO}_3 + 12\text{HF} = 3\text{SiF}_4 + 4\text{NO} + 8\text{H}_2\text{O}$	
$\text{Si} + \text{K}_2\text{CO}_3 = \text{K}_2\text{SiO}_3 + \text{C}$	Fused
$3\text{Si} + 2\text{N}_2 = \text{Si}_3\text{N}_4$	
$\text{Si} + 2\text{S} = \text{SiS}_2$	
$n\text{Si} + m\text{M} = \text{Si}_n\text{M}_m$	With many metals

**5. Silicides.**—Silicon dissolves in many molten metals, and the temperature-composition curves indicate the formation of both solid solutions and definite compounds. Compounds of the type,  $\text{M}_3\text{Si}$ , are formed by Li and Cu; of the type,  $\text{M}_2\text{Si}$ , by Mg, Mn, Fe, Co, Ni, and Pd; of the type,  $\text{MSi}$ , by Mn, Fe, Co, Ni, Pt, and Pd; of the type,  $\text{MSi}_2$ , by Ca, Co, Sr, V, and U; and of the type,  $\text{MSi}_3$ , by Co. A few of the more important compounds are discussed below.

**6. Ferrosilicon.**—FeSi is made by reducing siliceous iron ore in an electric furnace. It is employed extensively in the steel industry, especially in the manufacture of silicon steels, the more important of these being (1) acid resistant steel, e.g. "duriron" (16 per cent silicon) and (2) steel of high magnetic permeability. The addition of silicon to iron also reduces the amount of iron carbide,  $\text{Fe}_3\text{C}$ ; and thus converts white cast iron into grey cast iron. Silicon added to molten steel also serves as a "deoxidizing" agent.

**Hydrogenite**, a mixture of ferrosilicon and solid sodium hydroxide, evolves hydrogen

upon the addition of water, and has been used as a source of hydrogen for balloons and air ships.

**7. Silicon Carbide,  $\text{SiC}$ ,** is one of the hardest substances known. Although the data are somewhat indefinite, the arrangement of the atoms in the crystal appears to be a modified diamond type of structure. It is manufactured extensively for use as an abrasive, by heating a core of carbon packed in sand in an electric furnace:  $\text{SiO}_2 + 3\text{C} = \text{CSi} + 2\text{CO}$ . The furnace is of the resistance type, the carbon core serving as the heating element.

**8. Calcium Silicide,  $\text{CaSi}_2$ ,** is formed by heating lime, sand, and carbon in an electric furnace:  $\text{CaO} + 2\text{SiO}_2 + 5\text{C} = \text{CaSi}_2 + 5\text{CO}$ . It is a powerful reducing agent, and is employed as a "deoxidizing" agent in steel manufacture, and also as a reducing agent in certain explosives.

**9. Silicon and Hydrogen.**—The first 7 or 8 members of the series,  $\text{Si}_n\text{H}_{2n+2}$ , corresponding to the paraffin series, are known. These hydrogen compounds resemble the hydrocarbons in physical properties, but not in stability. They inflame spontaneously in air at room temperature, or

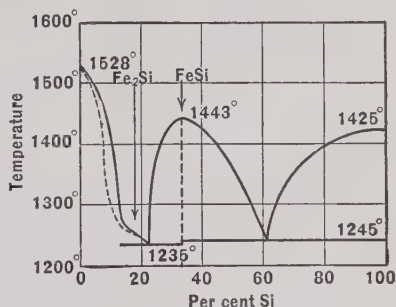


FIG. 2. Iron-silicon diagram.

slightly above, and are decomposed by alkali with the formation of a silicate and hydrogen. A mixture of the various members of the series results from the action of acids upon magnesium silicide,  $\text{Mg}_2\text{Si}$ , while lithium silicide,  $\text{Li}_3\text{Si}$ , gives largely silicoethane,  $\text{Si}_2\text{H}_6$ . The existence of unsaturated hydrogen compounds is doubtful, with the exception of the compound  $\text{SiH}_2$ .

**10. Silicon and the Halogens.**—The halogens react directly with silicon, forming tetrahalides. The energy of the reaction decreases with the increasing size of the halogens; with fluorine, the reaction is spontaneous at room temperature, while with iodine the reaction occurs only at red heat. The tetrahalides hydrolyze in water to form silicic acid and the hydrogen halide, and this hydrolysis is complete with all the tetrahalides, except the **tetrafluoride**. Due to the stability of the fluoride, silicon dioxide and most of the mineral silicates dissolve in hydrogen fluoride:  $\text{SiO}_2 + 4\text{HF} = \text{SiF}_4 + 2\text{H}_2\text{O}$ . The solid tetrafluoride sublimates without melting; but under a pressure of 2 atmospheres it melts at  $-77^\circ$ . At room temperature the tetrafluoride is a gas with a pungent odor. With water, partial hydrolysis results in the formation of **fluosilicic acid**:  $3\text{SiF}_4 + 3\text{H}_2\text{O} = 2\text{H}_2\text{SiF}_6 + \text{H}_2\text{SiO}_3$ . This is a moderately strong acid, and its potassium salt is but slightly soluble. X-ray data on the solid fluosilicates show that the six fluorine atoms are arranged symmetrically at equal distances about the silicon atom. In the acid nature of the fluoride, silicon again resembles boron.

**11. Silicon tetrachloride** is prepared by the action of chlorine on silicon carbide, or on a hot mixture of silica and carbon:  $2\text{Cl}_2 + \text{SiC} = \text{SiCl}_4 + \text{C}$ ;  $\text{SiO}_2 + 2\text{C} + 2\text{Cl}_2 = \text{SiCl}_4 + 2\text{CO}$ . The product prepared by these reactions also contains higher members of the series,  $\text{Si}_n\text{Cl}_{2n+2}$ . Mixtures of the tetrachloride and ammonia have been employed for the preparation of military smoke screens, since in moist air solid silicic acid and ammonium chloride are

formed. With sulfur trioxide, the oxychloride,  $\text{Si}_2\text{OCl}_6$ , and also silicon dioxide results:  $2\text{SiCl}_4 + 2\text{SO}_3 = \text{Si}_2\text{OCl}_6 + \text{S}_2\text{O}_5\text{Cl}_2$ , and  $\text{SiCl}_4 + 3\text{SO}_3 = \text{SiO}_2 + 2\text{S}_2\text{O}_5\text{Cl}_2$ .

**12.** By the action of hydrogen chloride upon heated silicon, chlorine hydrosilicons are formed, the most important being **silicochloroform**,  $\text{SiHCl}_3$ . This and other silicon hydrogen halides hydrolyze in water with the formation of oxyhydrogen compounds:  $2\text{SiH}_3\text{Cl} + \text{H}_2\text{O} = 2\text{HCl} + 2(\text{SiH}_3)_2\text{O}$  (Disiloxan):  $\text{SiH}_2\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + (\text{SiH}_2)_2\text{O}$  (Prosiloxan):  $\text{Si}_2\text{Cl}_6 + 4\text{H}_2\text{O} = 6\text{HCl} + (\text{SiO}_2\text{H})_2$  (Silico-oxalic acid);  $2\text{SiHCl}_3 + 3\text{H}_2\text{O} = 6\text{HCl} + \text{H}_2\text{Si}_2\text{O}_3$  (Silico-formic acid anhydride).

#### SILICON AND OXYGEN

**13. Silicon Monoxide.**—The yellowish brown monoxide,  $\text{SiO}$ , may be prepared by the reaction between carbon and excess silicon dioxide at temperatures around  $2000^\circ$ .  $\text{SiO}_2 + \text{C} = \text{SiO} + \text{CO}$ . The oxide is a solid at these temperatures, and unless rapidly cooled, decomposes:  $2\text{SiO} = \text{Si} + \text{SiO}_2$ . It is used commercially under the name **monox**, as a pigment, and also as an abrasive.

**14. Silicon Dioxide.**—Free silica,  $\text{SiO}_2$ , constitutes about 12 per cent of the earth's crust; and this, together with silica in combination with basic oxides, approximately 60 per cent. It occurs in three crystalline forms, quartz, tridymite, and cristobalite, and each of these has a number of modifications (Table III). It also exists as the supercooled liquid, or quartz glass. Sand, flint, and agate are familiar forms of silica. Kieselguhr, or diatomaceous earth, is silica resulting from the skeletons of diatoms.

Quartz belongs to the hexagonal system with threefold symmetry about its principal axis. The crystal has no plane or center of symmetry; and therefore exists in two forms called "right-handed" and "left-handed," which are mirror images of each other and rotate the plane of polarized light in opposite directions (Fig. 3). Crystals of enormous

size are occasionally found in nature. Quartz has a density of 2.65, and is somewhat harder than ordinary glass. It is very transparent over a range of wave-lengths extending from the infrared far into the ultraviolet (transmission

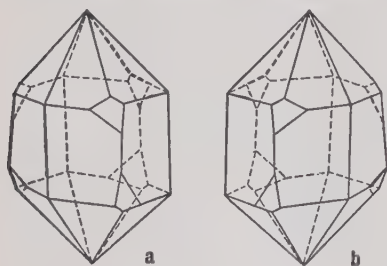


FIG. 3. Quartz crystals; a, right-handed; b, left-handed.

for 1 mm. thickness = 67 per cent at  $0.19 \mu$ ), and therefore finds considerable application in the manufacture of optical instruments and ultraviolet lamps.

As indicated in Table III, tridymite and cristobalite are unstable with respect to quartz at ordinary temperatures. The transition is slow at low temperatures, however, and both forms are found in nature, especially in lavas which have cooled quickly.

TABLE III  
MODIFICATIONS OF SILICA

	CRYSTAL SYSTEM	SPECIFIC GRAVITY	TRANSITION TEMPERATURE, °C.
$\alpha$ -Quartz.....	Hexagonal	2.65	575, to $\beta$ -Quartz
$\beta$ -Quartz.....	Hexagonal	2.63	870, to $\beta_2$ -Tridymite
$\alpha$ -Tridymite.....	Rhombic ?	2.28	117, to $\beta_1$ -Tridymite
$\beta_1$ -Tridymite.....	Hexagonal		163, to $\beta_2$ -Tridymite
$\beta_2$ -Tridymite.....	Hexagonal		1470, to $\beta$ -Cristobalite
$\alpha$ -Cristobalite.....	Tetragonal	2.35	225, to $\beta$ -Cristobalite
$\beta$ -Cristobalite.....	Cubic	2.21	1710, to liquid
Silica glass.....	Amorphous	2.21	

Liquid silica is highly viscous, and like all such liquids, readily supercools. Quartz glass has a lower density (2.2) than the crystals, and a very small coefficient of expansion, 0.0<sub>6</sub>54 (linear). Because of its low expansion, it is possible to plunge white hot quartz glass into water without having it crack. Quartz glass does not soften below 1500°, whereas



ordinary glass softens around 600 to 900°. Both of these qualities make it very valuable in the construction of apparatus for high temperature measurements. It should be noted, however, that helium and hydrogen diffuse rather readily through quartz glass at temperatures as low as 300°. Quartz glass is now manufactured by fusing pure silica in a high temperature furnace.

The crystal structure of the three forms of silica may be represented as tetrahedral groups of oxygen atoms about a central silicon atom. The tetrahedra are linked at each corner so that each oxygen is attached to two silicons. The high temperature or  $\beta$ -modifications have a more definite structure and higher symmetry than the  $\alpha$ -forms.  $\beta$ -tridymite is similar to the wurtzite structure and  $\beta$ -cristobalite to the sphalerite structure, i.e., the silicon atoms are arranged like the carbon atoms of diamond. In  $\beta$ -quartz the tetrahedra are more closely packed. In the unit cell the silicons are located in three planes at different heights and the projection of the centers onto a single plane gives a hexagonal pattern, Fig. 4.

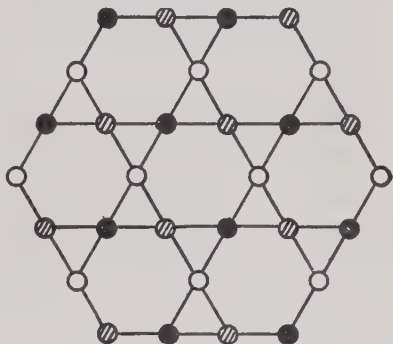


FIG. 4. Projection of silicon atoms in  $\beta$ -quartz.

The various forms of silica are soluble in alkalis with the formation of silicates, but they are only slightly affected by acids, except hydrofluoric which converts silica into the tetrafluoride. The great stability of silicon dioxide is related to its high heat of formation:  $\text{Si} + \text{O}_2 = \text{SiO}_2 + 200 \text{ kcal.}$  It is exceeded by that of the fluoride, however:  $\text{Si} + 2\text{F}_2 = \text{SiF}_4 + 360 \text{ kcal.}$

**15. Silicic Acids.**—The result of the addition of a strong acid to a soluble silicate is the formation of a colloidal solu-

tion, or hydrogel, of the general formula,  $m\text{SiO}_2 \cdot n\text{H}_2\text{O}$ . Upon heating, the gel may be gradually dehydrated and the dioxide formed. Partially dehydrated gels have high absorbent power, and are now used commercially in the absorption of benzene, sulfur dioxide, nitric acid, nitrogen dioxide, and other vapors. Many forms of hydrated silica occur in nature, such as opal.

Salts and mineral derivatives of a large number of silicic acids are known. The nomenclature of these hypothetical acids is indicated in Table IV.

TABLE IV  
SILICIC ACIDS

	Mono- $m\text{H}_2\text{O} \cdot \text{SiO}_2$	Di- $m\text{H}_2\text{O} \cdot 2\text{SiO}_2$	Tri- $m\text{H}_2\text{O} \cdot 3\text{SiO}_2$	Tetra- $m\text{H}_2\text{O} \cdot 4\text{SiO}_2$
Ortho-.....	$\text{H}_4\text{SiO}_4$	$\text{H}_6\text{Si}_2\text{O}_7$	$\text{H}_8\text{Si}_3\text{O}_{10}$	$\text{H}_{10}\text{Si}_4\text{O}_{13}$
Meta-.....	$\text{H}_2\text{SiO}_3$	$(\text{H}_2\text{SiO}_3)_2$	$(\text{H}_2\text{SiO}_3)_3$	$(\text{H}_2\text{SiO}_3)_4$
Meso-.....	—	$\text{H}_2\text{Si}_2\text{O}_5$	$\text{H}_4\text{Si}_3\text{O}_8$	$\text{H}_6\text{Si}_4\text{O}_{11}$
Para-.....	—	—	$\text{H}_2\text{Si}_3\text{O}_7$	$\text{H}_4\text{Si}_4\text{O}_{10}$
Tertero-.....	—	—	—	$\text{H}_2\text{Si}_4\text{O}_9$

**16. Alkali Silicates.**—Commercial sodium silicate, known as **water glass**, is made by fusing sand, flint, or kieselguhr with sodium carbonate and charcoal, and extracting the glassy mass in an autoclave, or by dissolving the silica in sodium hydroxide. The product has a ratio of  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$ , between 2 and 4, and is usually sold in concentrated solution as a syrupy liquid.

Water glass is used in soaps and washing powders to provide an alkaline reaction. It is used: for fireproofing materials; in paper manufacturing as sizing; as an egg-preserved; and as a mineral glue for cementing wood, glass, porcelain, etc. Solid sodium metasilicate,  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ , orthosilicate,  $\text{Na}_4\text{SiO}_4$ , and "sesqui" silicate  $\text{Na}_3\text{HSiO}_4 \cdot 5\text{H}_2\text{O}$  are commercial products, used as water softeners and cleaning agents.

The other alkali silicates resemble the sodium compound.

Temperature-composition curves for the system,  $\text{K}_2\text{O-SiO}_2\text{-H}_2\text{O}$ , show many hydrates of the salts,  $\text{K}_2\text{SiO}_3$  and  $\text{K}_2\text{Si}_2\text{O}_5$ , and lithium forms the ortho salt,  $\text{Li}_4\text{SiO}_4$ . Although silica is soluble in concentrated ammonia, solid ammonium silicates cannot be prepared, as the solutions hydrolyze completely when evaporated.

**17. Mineral Silicates.**—Rocks may be classified as (1) igneous, (2) sedimentary, (3) metamorphic. Igneous rocks have resulted from the solidification of the earth's molten magma. Sedimentary rocks are formed from the igneous by the action of weathering agents, followed by sedimentation under water, e.g. sandstone. Certain igneous and sedimentary rocks have been subjected to heat, pressure, or solvent action, and are thereby modified to form the metamorphic rocks, e.g. serpentine.

Analysis of a number of the more common igneous rocks gives the ranges in composition summarized in Table V for the component oxides:

TABLE V  
COMPOSITION OF IGNEOUS ROCKS

Oxide . . . .	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{MgO}$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{H}_2\text{O}$
Per cent . . .	40-75	7-18	0.2-8	0.3-14	0.1-24	0.2-15	1-5	1-8	0.5-4

The most abundant igneous rock is **granite**, a mixture of feldspar (Table VI), mica, and quartz. **Rhyolite** and **obsidian** have the same general composition as granite, but the former has cooled much more rapidly and its individual crystals are much smaller than those in granite. Obsidian is a volcanic glass. Next to granite, the most important igneous rocks are the ferromagnesium silicates, the pyroxenes, and amphiboles. The continents appear to be slabs of granite about 20 miles thick "floating" on heavier basaltic material. The composition of basalt is largely calcium, magnesium, and iron silicate.

**18. Feldspar**,  $\text{KAlSi}_3\text{O}_8$ , is the most abundant of all minerals on the earth's crust. The sodium and calcium feldspars are isomorphous. Large quantities of feldspar are used in the ceramic industries (see Pottery). Feldspar is converted by the action of carbon dioxide and water into (1) mica or by further action into (2) kaolinite (clay): (1)  $3\text{KAlSi}_3\text{O}_8 + \text{H}_2\text{CO}_3 = \text{KH}_2\text{Al}_3\text{Si}_3\text{O}_{12} + 6\text{SiO}_2 + \text{K}_2\text{CO}_3$ ; (2)  $2\text{KAlSi}_3\text{O}_8 + 2\text{H}_2\text{O} + \text{CO}_2 = \text{H}_4\text{Al}_2\text{Si}_2\text{O}_9 + \text{K}_2\text{CO}_3 + 4\text{SiO}_2$ .

**19. The micas** are acid orthosilicates of aluminum with magnesium, ferrous iron, and the alkalis. Their most striking characteristic is cleavage into very thin elastic transparent sheets. Mica is used extensively in the electrical industries as an insulator. It is used in making windows for stoves, in lamp chimneys, as Christmas tree "snow," as a decorative material for wall paper, and in many special paints. When heated, mica breaks down into **leucite**:  $\text{KH}_2\text{Al}_3(\text{SiO}_4)_3 = \text{KAl}(\text{SiO}_3)_2 + \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{H}_2\text{O}$ .

**20. The term asbestos** includes several of the magnesium silicates, e.g. **amphibole** and **olivine**. These minerals have a fibrous structure, silky luster, and are difficultly fusible. Asbestos is important commercially as a thermal insulator. The long fibers permit the manufacture of asbestos yarn, cloth, and paper, and from these innumerable fireproof objects. Mixtures of asbestos and Portland cement are used in fireproof shingles.

**21. Kaolin**, impure kaolinite, or **clay**, is a hydrated aluminum silicate, and **talc**, or **soapstone**, is a hydrated magnesium silicate. Clay is further discussed under pottery. Talc is used in soap, French chalk, talcum powder; and in paint, roofing, and rubber. A fibrous form is used extensively in paper. Soapstone is used as a refractory material. The bentonites and the pyrophyllites are forms of aluminum silicates or the clay minerals. Both are important as commercial fillers for rubber, paper, and soaps.

TABLE VI

## MINERAL SILICATES

Feldspars	{ Orthoclase, $\text{KAlSi}_3\text{O}_8$ (monosymmetric)
	{ Microcline, $\text{KAlSi}_3\text{O}_8$ (anorthic)
	{ Anorthoclase, $\text{NaAlSi}_3\text{O}_8$ (anorthic)
	{ Plagioclase, $n(\text{NaAlSi}_3\text{O}_8)m(\text{CaAl}_2\text{Si}_2\text{O}_8)$
Feldspathoid group	{ Leucite, $\text{KAl}(\text{SiO}_3)_2$
	{ Nepheline, $[\text{Na}, \text{K}]\text{AlSiO}_4$
	{ Sodalite, $\text{Na}_8\text{Al}_6\text{Cl}_2(\text{Si}_6\text{O}_{24})$
	{ Lazurite, $\text{Na}_5\text{Al}_3\text{S}(\text{SiO}_4)_3$
Pyroxene (Cleavage $87^\circ$ and $93^\circ$ )	{ Enstatite, $\text{MgSiO}_4$
	{ Hypersthene, $[\text{Mg}, \text{Fe}]\text{SiO}_3$
	{ Diopside, $\text{Ca}[\text{Mg}, \text{Fe}](\text{SiO}_3)_2$
	{ Augite, $\text{CaMg}(\text{SiO}_3)_2 + [\text{Mg}, \text{Fe}][\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3](\text{SiO}_3)$
	{ Jadeite, $\text{NaAl}(\text{SiO}_3)_2$
Amphibole (Cleavage $56^\circ$ and $124^\circ$ )	{ Anthophyllite, $(\text{OH})_2(\text{Mg}, \text{Fe})_7\text{Si}_8\text{O}_{22}$
	{ Tremolite, $(\text{OH})_2\text{Ca}_2[\text{Mg}, \text{Fe}]_5\text{Si}_8\text{O}_{22}$
	{ Hornblende, $(\text{OH})_2(\text{Ca}, \text{Na}, \text{K})_{2-3}(\text{Mg}, \text{Fe}, \text{Al})_5(\text{Si}, \text{Al})_2\text{Si}_6\text{O}_{22}$
	{ Glaucophanite, $(\text{OH})_2\text{Na}_2(\text{Fe}, \text{Mg})_3(\text{Al}, \text{Fe})_2\text{Si}_8\text{O}_{22}$
	{ Vesuvianite, $\text{Ca}_{10}\text{Al}_4(\text{Mg}, \text{Fe})_2\text{Si}_9\text{O}_{34}(\text{OH})_4$
Complex calcium aluminum silicates	{ Epidote, $\text{Ca}_2(\text{Al}, \text{Fe})_3\text{OH}(\text{SiO}_4)_2$
	{ Prehnite, $\text{H}_2\text{Ca}_2\text{Al}_2(\text{SiO}_4)_3$
	{ Scapolite, $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4, \text{CO}_3)$ to $\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}$
	{ Muscovite, $(\text{OH})_2\text{KAl}_2\text{Si}_3\text{AlO}_{10}$
Mica and Talc	{ Biotite, $(\text{OH})_2\text{K}(\text{Mg}, \text{Fe})_3\text{AlSi}_3\text{O}_{10}$
	{ Phlogopite, $(\text{OH})_2\text{KMg}_3\text{Si}_2\text{AlO}_{10}$
	{ Lepidolite, $\text{KLi}_2\text{Al}(\text{Si}_4\text{O}_{10})(\text{OH}, \text{F})_2$
	{ Talc, $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$
Zeolites	{ Heulandite, $\text{CaAl}_2\text{Si}_7\text{O}_{18} \cdot 6\text{H}_2\text{O}$
	{ Stilbite, $(\text{Na}_2\text{Ca})\text{Al}_2\text{Si}_6\text{O}_{16} \cdot 6\text{H}_2\text{O}$
	{ Chabazite, $[\text{Ca}, \text{Na}_2]\text{Al}_2(\text{SiO}_3)_4 \cdot 6\text{H}_2\text{O}$
	{ Analcite, $\text{NaAl}(\text{SiO}_3)_2 \cdot \text{H}_2\text{O}$
Chlorit	{ Natrolite, $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$
	{ Clinocllore, $\text{Al}, \text{Mg}_5\text{Si}_3\text{Al}_{10}(\text{OH})_8$
	{ Penninite, $\text{Mg}_5(\text{Al}, \text{Fe})(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_8$
	{ Chrysocolla, $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$
Miscellaneous Metasilicates	{ Serpentine, $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$ , or $(\text{OH})_6\text{Mg}_6\text{SiO}_4\text{O}_{11} \cdot \text{H}_2\text{O}$
	{ Beryl, $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$
	{ Spodumene, $\text{LiAl}(\text{SiO}_3)_2$
	{ Calamine, $\text{Zn}_2(\text{OH})_2\text{SiO}_3$
	{ Willemite, $\text{Zn}_2\text{SiO}_4$
	{ Zircon, $\text{ZrSiO}_4$
Miscellaneous Silicates	{ Kaolinite, $\text{Al}_2(\text{Si}_2\text{O}_3)(\text{OH})_4$
	{ Andalusite, $\text{Al}_2\text{SiO}_3$
	{ Cyanite, $\text{Al}_2\text{SiO}_5$
	{ Sillimanite, $\text{Al}_2\text{SiO}_5$
	{ Topaz, $(\text{AlF})_2\text{SiO}_4$
	{ Titanite, $\text{CaTiSiO}_5$

TABLE VI. (*Cont'd*)

## MINERAL SILICATES

Borosilicates	{	Tourmaline, $(\text{Na}_2\text{Ca})(\text{Mg}, \text{Al})_{27}\text{B}_9\text{Si}_{18}\text{H}_x\text{O}_{93}$
		Datolite, $\text{CaB}(\text{OH})\text{SiO}_4$
		Axinite, $\text{HCa}_2(\text{Fe}, \text{Mn})\text{Al}_2\text{B}(\text{SiO}_4)_4$
Garnet	{	Grossularite, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$
		Almandite, $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$
		Pyrope, $\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$
		Andradite, $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$
Olivine group	{	Olivine, $(\text{Mg}, \text{Fe})_2\text{SiO}_4$
		Forsterite, $\text{Mg}_2\text{SiO}_4$

**22. Structure of Silicate Minerals.**—The tetrahedron of oxygen atoms with a silicon at the center, which occurs in silica (Par. 14), is a general characteristic of all silicate minerals. In the orthosilicates such as zircon,  $\text{ZrSiO}_4$ , and olivine,  $(\text{Mg}, \text{Fe})_2\text{SiO}_4$ , the crystal is a lattice of  $\text{SiO}_4$  tetrahedra and the positive ions; and the same is true of the orthosilicates, the negative ion,  $\text{Si}_2\text{O}_7^{-6}$ , consisting of two tetrahedra linked by a corner. The metasilicates ( $\text{SiO}_3^{--}$  radical) may complete the tetrahedron of oxygen atoms by forming rings in which two corners of each tetrahedron are shared. The most common ring contains six tetrahedra, for example beryl,  $\text{Be}_2\text{Al}_2\text{Si}_6\text{O}_{18}$ , consists of a lattice of the posi-

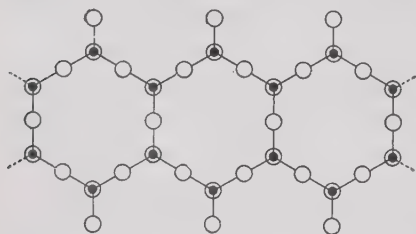


FIG. 5. Chains in the amphiboles.

tive ions with the ring-like negative ions  $\text{Si}_6\text{O}_{18}^{-12}$ . A three membered ring is also known in benitoite,  $\text{BaTiSi}_3\text{O}_9$ . In the pyroxenes, e.g.,  $\text{CaMg}(\text{SiO}_3)_2$ , which are also metasilicates, the  $\text{SiO}_3$  groups

form infinite chains instead of rings, and the positive ions serve to bind the chains together. The amphiboles contain infinite double chains formed from the  $\text{Si}_4\text{O}_{11}^{-6}$  groups. These are illustrated in Fig. 5. In the various types of asbestos these chains are in bundles of parallel fibers. In other cases they form sheets of matted fibers. Jade



appears to be a mineral in which the fibers are matted in all directions.

Silicates containing the  $\text{Si}_4\text{O}_{10}^{-4}$  group (or  $\text{AlSi}_3\text{O}_{10}^{-5}$  if one Si is replaced by Al) form infinite sheets of silicon oxygen tetrahedra. These may be looked upon as two dimensional extensions of the arrangement shown in Fig. 5 to give a sheet with the appearance of a wire netting. Such sheets held together by positive ions are found in the clay minerals. Double sheets with the vertices of the tetrahedra pointing toward each other occur in the mica minerals and talc. In the former the sheets are held together by alkali or alkaline earth ions, but the latter contains no intermediate atoms. In the chlorite the mica-like sheets are separated by intermediate magnesium-aluminum oxide layers.

Silica has been given as an example of a three-dimensional network of silicon-oxygen tetrahedra. If one out of every four silicons in the structure is replaced by KAl, the resulting feldspar, e.g.,  $\text{KAlSi}_3\text{O}_8$ , is a network of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra. The negative charge is neutralized by the potassium ions which occupy holes in the structure. In addition to the feldspar group the zeolite minerals have a three-dimensional framework. These structures are, however, more open with large cavities and channels. They are capable of holding large amounts of water which may be driven off readily, and the positive ions which are contained in the cavities and balance the negative charge on the framework are readily replaceable by other ions.

**23. Pottery and Porcelain.**—Mixtures of clay (kaolinite), quartz, and feldspar, in various proportions and baked at various temperatures, form an extensive series of ceramic products. Most types of pottery or bricks are made from naturally occurring clays, which contain sand and feldspar. They are usually colored buff or red by iron oxide, the white porcelain clays being relatively scarce. Upon heating, kaolin is altered, probably losing water, according to the equation:  $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9 = \text{Al}_2\text{SiO}_5 + \text{SiO}_2$

+  $2\text{H}_2\text{O}$ ; and around  $1200^\circ$  the feldspar fuses and serves to bind the clay and quartz together. The properties of the earthenware depend to a great extent upon the temperature at which it is baked, and there is often but slight variation in composition between different types of products. Soft porcelain contains a high per cent of calcium phosphate. Glaze is imparted to the cheaper grades of pottery by the introduction of sodium chloride near the end of the firing. Other glazes used are fusible lead calcium aluminoborosilicates, or, in many cases, simple feldspar.

**24. Glass.**—Glass is a fused non-crystalline mixture of basic oxides and silicon dioxide. The basic oxides are usually the alkalis and alkaline earths, but they may be substituted in whole or in part by oxides of lead, zinc, arsenic, antimony, aluminum, etc.; and the silicon dioxide by boric or phosphoric oxides. Like all super-cooled liquids, glass does not have a definite melting point, but softens gradually over a range of temperatures. In this viscous state, glass may be blown or rolled into almost any desired shape or form. The raw materials which are fused together to form glass are sand, or the other acid oxides, and generally the carbonates of the basic constituents.

The manufacture of common **soda glass** is often represented by the equation,  $2\text{Na}_2\text{CO}_3 + \text{CaCO}_3 + 6\text{SiO}_2 = \text{Na}_4\text{CaSi}_6\text{O}_{15} + 3\text{CO}_2$ , but the product cannot be considered as a definite compound. It is used in making bottles, window glass, glass tubing, etc. The percentage composition of soda glass is approximately:  $\text{SiO}_2$ , 71–78;  $\text{Na}_2\text{O}$ , 12–17;  $\text{CaO}$ , 5–15;  $\text{Al}_2\text{O}_3$ , 1–4. The corresponding **potash glass**, also called **hard glass**, or **Bohemian glass**, has a higher fusing temperature. **Potash-lead glass**, or **flint glass**, has a high density and index of refraction, and is used in making cut glass articles. **Pyrex glass** is very high in the acid oxides:  $\text{SiO}_2$ , 80 per cent,  $\text{B}_2\text{O}_3$ , 12 per cent, with the balance  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$ . It has a low coefficient of expansion, and is, therefore, very suitable for articles sub-

ject to sudden changes in temperature. It is also resistant to chemical action. **Jena glass** is a zinc-barium borosilicate.

Glass may be colored by the presence of small amounts of metal oxides: chromium or copper giving green; cobalt, blue; manganese, violet. A colloidal metal suspension of gold gives ruby glass. "Milk glass" usually contains stannic oxide or calcium fluoride.

If glass is held at a high temperature for a long time, a certain amount of crystallization may occur (called devitrification). Thick glass objects must be carefully annealed, i.e. cooled very slowly, as the cooling of the outer portions more rapidly than the interior will result in great strains and the subsequent cracking of the object.

**25. Portland Cement.**—Although lime mortars have been used for centuries, the modern hydraulic cement dates back only to about 1825, and its extensive use to about 1900. The approximate composition of Portland cement is given in Table VII.

TABLE VII  
COMPOSITION OF PORTLAND CEMENT

Oxide . . . . .	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	Na <sub>2</sub> O, K <sub>2</sub> O
Per cent . . . . .	58-67	19-26	4-11	2-5	0-5	0-2.5	0-3

Cement is made by heating a mixture of limestone and clay, or material of equivalent composition, to the point of incipient fusion (about 1450° C.). The product, termed clinker, is ground with 2-3 per cent of gypsum, added to decrease the time of setting, to give the cement.

The chemical composition appears to be largely the three compounds, Ca<sub>2</sub>SiO<sub>4</sub>, Ca<sub>3</sub>SiO<sub>5</sub>, and Ca<sub>3</sub>(AlO<sub>3</sub>)<sub>2</sub>. Setting occurs upon the addition of water, and is due to the hydration of these compounds. In this action, the tricalcium silicate appears to be especially important, as it forms ge-

latinous hydrates which gradually harden and cement the crystals together.

The production of cement in the United States in 1938 was about 100 million barrels. The major portion of this was used in mixture with crushed rock and sand to make **concrete**.

**26. Silicate Analysis.**—In detecting the presence of silicon, advantage is taken of the volatility of silicon tetrafluoride. The sample is heated with hydrofluoric acid in a lead or platinum dish. If silicon is present, a drop of water in a wire loop, placed in the fumes, becomes cloudy owing to the formation of silicic acid:  $3\text{SiF}_4 + 3\text{H}_2\text{O} = \text{H}_2\text{SiO}_3 + 2\text{H}_2\text{SiF}_6$ .

Silicates are determined quantitatively by gravimetric methods, generally separating silicon dioxide and weighing as such. In this process, decomposition of the silicate may often be accomplished by digesting with concentrated hydrochloric acid, leaving a residue of silica. Other silicates must first be fused with sodium carbonate before they can be decomposed by acid. The silica residue may be contaminated with  $\text{BaSO}_4$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ , and oxides of certain rare elements; the amount in the mixture is often determined by heating with hydrofluoric acid, obtaining the silica by loss of weight, due to the volatilization of the tetrafluoride.

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## Chapter XV

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### THE METALS OF GROUP IV. TITANIUM, ZIRCONIUM, HAFNIUM, THORIUM, AND GERMANIUM, TIN, LEAD

1. The first and second elements of Group IV, carbon and silicon, have been discussed in the two preceding chapters. The remaining elements of the main group are titanium, zirconium, hafnium, and thorium, and of the subgroup, germanium, tin, and lead. All of the free elements are metals, but both branches of the group show many similarities to silicon in their chemical properties.

Titanium and the heavier elements of the main group are each the second elements of a transition series in which the kernel is being transformed from the noble gas structure to the eighteen electron type (Append. XVIII). However, the two *d* electrons are easily removed so that all members of the group show the characteristic + 4 oxidation state. Titanium has also a fairly stable + 3 and a less stable + 2 state.

The subgroup elements form compounds of both the + 2 and + 4 states, the former becoming increasingly stable with respect to the latter with increasing atomic weight.

The tetroxides of all the elements, except thorium, are amphoteric, and those of the main group are, in general, somewhat more basic than the oxides of the corresponding elements of the subgroup, which is in agreement with a slightly larger size of the main group ions, and in both

groups the basic character increases with increasing size. Like silicon, all of the members of the group form complex fluorides, and all the tetrachlorides, except thorium, are volatile liquids.

One of the most striking differences between the two branches of the group is the much greater stability of the sulfides of germanium, tin, and lead. This stability of the sulfides is a general characteristic of the ions with eighteen electrons in the outer shell of the kernel (cf. VII—2). The elements of Subgroup IV resemble those of Subgroup III in not forming complex ions with ammonia.

Cerium is often discussed in connection with Group IV, but it should be included in the rare earths, although it does form a dioxide which resembles in many respects the dioxides of zirconium and thorium.

## TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM

**2. Occurrence.**—The elements of this group are by no means as rare as they have commonly been considered. Titanium ranks eighth among the metals in order of abundance in the igneous rocks, the per cent of the element present in the earth's crust being estimated at 0.43. The values for the other elements of the group are: zirconium, 0.026; hafnium,  $3 \times 10^{-5}$ ; and thorium,  $2 \times 10^{-5}$ .

The elements do not occur free, but their compounds are widely distributed in nature. Because of the similarity in chemical behavior between these elements and silicon, their presence in rocks is often overlooked.

The most important titanium ores are **ilmenite**,  $\text{FeTiO}_3$ , **rutile**,  $\text{TiO}_2$ , and **arizonite**,  $\text{Fe}_2\text{O}_3 \cdot 3\text{TiO}_2$ . Metatitanates of ferric iron, calcium, magnesium, manganese, and lead, also occur. Titanosilicates such as **sphene**,  $\text{CaTiSiO}_5$ , are common, and less frequently borotitanates and titanoantimonates. The annual world production of the oxide is about 225,000 tons: the major portion is consumed in the manu-



facture of white pigments. The sand of certain beaches in India is the principal commercial source.

Zirconium occurs principally as **baddeleyite**,  $\text{ZrO}_2$ , and **zircon**,  $\text{ZrSiO}_4$ , the most extensive deposits being located in Brazil. Complex zirconates, often containing the other members of the group, are also found. Hafnium is present to the extent of 1 or 2 per cent in practically all primary zirconium minerals. Thorium orthosilicate,  $\text{ThSiO}_4$ , or possibly  $\text{ThO}_2 \cdot \text{SiO}_2$ , occurs as the black mineral **thorite** and also as the orange colored mineral **orangite**. These thorium ores and also the mineral **thorianite**,  $\text{ThO}_2$ , frequently contain uranium oxides,  $\text{UO}_2$  and  $\text{U}_2\text{O}_3$ . The principal source of commercial thorium is monazite sand (see Rare Earths).

**3. The Metals.**—The electro-positive nature of the elements, together with their great tendency to form carbides, nitrides, and silicides at high temperatures, renders the preparation of the metals extremely difficult. The reduction of the chlorides or potassium complex fluorides by heating with sodium in steel bombs gives a comparatively pure product. The Goldschmidt reduction with aluminum gives aluminum alloys. In the case of titanium, the alloy contains 5 or 6 per cent aluminum, but if iron is present, the product is largely ferro-titanium. Zirconium may be separated from the aluminum alloy by distillation. The reduction of titanium dioxide by carbon in an electric furnace yields a mixture of the metal and carbide. Ferro-carbon-titanium is made by the reduction of mixtures of iron and titanium oxides. Thorium is best prepared by reduction of the dioxide with calcium in the presence of calcium chloride in a bomb, and by the electrolysis of the fused complex fluoride  $\text{K}_2\text{ThF}_6$ .

The lighter metals are described as hard and brittle, though these properties may be due, in part, to the presence of impurities. Thorium is soft and malleable. The metals titanium, zirconium, and hafnium appear to have the hex-

TABLE I  
ATOMS AND PHYSICAL PROPERTIES

	Ti	Zr	Hf	Th
Atomic weight . . . . .	47.90	91.22	178.6	232.12
Atomic number . . . . .	22	40	72	90
Isotopes . . . . .	46, 47, 48, 49, 50	90, 91, 92, 94, 96	176, 177, 178, 179, 180	(228) (230) (232) (234)
Melting point, ° C. . . . .	1800	1700	1700	1845
Boiling point, ° C. . . . .	> 3000	> 2900	> 3200	> 3000
Density . . . . .	4.5	6.4	11.4	11.2
Electrical resistivity, ohm-cm. . . . .	$3 \times 10^{-6}$	$170 \times 10^{-6}$	—	$18 \times 10^{-6}$
Radius of $M^{+4}$ ion in crystals, cm. $\times 10^8$ . . . . .	0.68	0.80	—	1.1

agonal close packed form of crystal lattice, while thorium has a face centered cubic lattice. Titanium is almost as good an electrical conductor as aluminum.

There are practically no commercial uses of the pure metals. Ferrotitanium is used extensively in the steel industry; the titanium is considered extremely valuable in removing nitrogen (by forming nitride) from, and in imparting toughness to steel. Ferrozirconium is an excellent scavenger for oxygen and sulfur and also improves the grain size in steel.

**4. Reactions of the Metals.**—The reactions of the metals are summarized in Table II. At ordinary temperatures, they are not very reactive, being oxidized but slowly by

TABLE II  
REACTIONS OF Ti, Zr, Hf, AND Th

$M + O_2 = MO_2$	Burn when heated
$M + 2X_2 = MX_4$	With halogens when heated
$M + 2H_2O = MO_2 + 2H_2$	With steam
$M + 4HF = MF_4 + 2H_2$	Not rapid with Th
$M + 4HCl = MCl_4 + 2H_2$	With hot concentrated acid, but Ti gives $TiCl_3$
$M + H_2 = MH_2$	$TiH_2$ doubtful. Th gives $ThH_4$
$M + 2S = MS_2$	Also react with P, C, B, and Si at high temperatures
$3M + 2N_2 = M_3N_4$	Also MN
$M + 2H_2O = MO_2 + 4H^+ + 4e^-$	Potential in volts, Ti, 0.95; Zr, 1.43; Th, 1.80; Hf, 1.57

oxygen or by hydrogen ion. Measurements of the electrode potentials of the group are unreliable because of the difficulties in obtaining equilibrium conditions. In spite of its highly electropositive character zirconium is not readily soluble in nitric acid.

## TITANIUM COMPOUNDS

**5. Oxidation States.**—Titanium forms compounds in which it has the oxidation states of + 2, + 3, and + 4. Important oxidation-reduction potentials relating the states are given below:

	VOLTS
$\text{Ti} = \text{Ti}^{++} + 2e^-$ .....	1.75
$\text{Ti}^{++} = \text{Ti}^{+++} + e^-$ .....	0.37
$\text{H}_2\text{O} + \text{Ti}^{+++} = \text{TiO}^{++} + 2\text{H}^+ + e^-$ .....	0.1
$6\text{F}^- + \text{Ti} = \text{TiF}_6^{--} + 4e^-$ .....	1.24

**6. The + 2 State.**—The **oxide**,  $\text{TiO}$ , is prepared by the high temperature reduction of the dioxide by carbon or magnesium. It is basic, but its salts are readily oxidized in solution by hydrogen ion unless the acid concentration is very low. The **dichloride** may be formed at high temperatures by the decomposition of the trichloride:  $2\text{TiCl}_3 = \text{TiCl}_2 + \text{TiCl}_4$ .

**7. Compounds of the + 3 State.**—The **sesquioxide** is formed in the reaction:  $2\text{TiO}_2 + \text{H}_2 = \text{Ti}_2\text{O}_3 + \text{H}_2\text{O}$ . It also is basic. The corresponding **titanous hydroxide**,  $\text{Ti}(\text{OH})_3$ , is precipitated upon the addition of alkalis to titanous salts in solution. This hydroxide is a very powerful reducing agent (Par. 5). It evolves hydrogen to form the dioxide:  $\text{Ti}(\text{OH})_3 = \text{TiO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{H}_2$ ; and reduces nitrate in alkaline solution to ammonia:  $8\text{Ti}(\text{OH})_3 + \text{NO}_3^- = \text{NH}_3 + 8\text{TiO}_2 + \text{OH}^- + 10\text{H}_2\text{O}$ . Anhydrous **trihalides** may be prepared by reducing the tetrahalides at moderately high temperatures, e.g.,  $\text{TiCl}_4 + \text{Ag} = \text{TiCl}_3 + \text{AgCl}$ .

Solutions of titanous ion,  $\text{Ti}^{+++}$ , are readily prepared from solutions of titanous salts by electrolytic reduction, or

by the reducing action of zinc upon the hot solution. Titanous solutions are violet. Titanous solutions are important as volumetric reagents, as they are oxidized quantitatively by many oxidizing agents, e.g.,  $\text{Fe}^{+++}$  and  $\text{MnO}_4^-$ . Titanous ion is much less hydrolyzed than the titanic ion. The formation of the slightly soluble hydroxide has been discussed above. The cesium titanous alum,  $\text{CsTi}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , is but sparingly soluble.

**8. Compounds of the + 4 State.**—The **dioxide** occurs in nature in two tetragonal forms, **rutile** and **anatase**, and also in a rhombic form called brookite. The pure oxide is white, but natural rutile is usually brown or black. The arrangement of the atoms in the rutile crystal lattice is given in Appendix V. This is the common crystal form of compounds  $\text{MX}_2$  when the ratio of the diameter of M to X is  $< 0.6$ . When this ratio is greater, the arrangement is generally that of fluorite.

The fused oxide is difficult to dissolve, but the hydrated forms dissolve readily in acids and slightly in alkalis. However, the chemistry of the titanium minerals is essentially that of an acid oxide. The oxide fused with metal oxides or carbonates yields **titanates**, e.g.  $\text{CaTiO}_3$ ,  $\text{Ba}_2\text{Ti}_3\text{O}_8$ ,  $\text{ZnTiO}_3$ ,  $\text{Zn}_2\text{TiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{Mn}_2\text{TiO}_4$ . The potassium metatitanate,  $\text{K}_2\text{TiO}_3$ , is soluble in cold water, but upon boiling, the titanium is completely precipitated as the dioxide. The dioxide has become one of the most important white pigments. It is used in ceramics to make a yellow glassware. The hydrous oxide is an important mordant.

When an acid solution of a titanium salt is made alkaline, a hydrogel is formed. Upon aging, the gel gives an X-ray pattern corresponding to that of anatase. Hydrous oxide formed by the hydrolysis of  $\text{TiCl}_4$  appears to be the rutile modification. The precipitated gel, often referred to as ortho- or  $\alpha$ -titanic acid, is readily soluble in acids. So-called meta- or  $\beta$ -titanic acid, an insoluble form, is obtained

by the action of nitric acid upon the metal. (Cf. similar stannic acids.)

The addition of hydrogen peroxide to a solution of the sulfate yields the complex orange peroxy ion  $\text{TiO}_2(\text{SO}_4)_2^{--}$ . The peroxy-acid,  $\text{H}_4\text{TiO}_5$  has been precipitated from ammonia solutions and the salt  $\text{K}_4\text{TiO}_8$  is known.

9. The anhydrous **halides** are prepared by direct reaction of the elements, or by the action of the halogen upon heated mixtures of the oxide and carbon, e.g.  $\text{TiO}_2 + \text{C} + 2\text{Cl}_2 = \text{TiCl}_4 + \text{CO}_2$ . Water solutions are prepared by dissolving the hydrated oxide in concentrated hydrohalic acid, but in dilute acid the halides readily hydrolyze to the dioxide. The tetrachloride is employed for producing smoke screens. The smoke particles are largely  $\text{TiCl}_4 \cdot 5\text{H}_2\text{O}$ . The lighter halides form complex ions, e.g.,  $\text{TiF}_6^{--}$  and  $\text{TiCl}_6^{--}$ . **Potassium fluorotitanate**,  $\text{K}_2\text{TiF}_6$ , is but slightly soluble.

10. The hydrated **dioxide** dissolves in sulfuric acid solutions. In dilute acid, the sulfate hydrolyzes to form **basic sulfates**, e.g.,  $\text{Ti}_2\text{O}(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$  and  $\text{TiO} \cdot \text{SO}_4 \cdot n\text{H}_2\text{O}$ . Similarly **basic nitrates** and **phosphates** exist, and the phosphates form a number of double basic compounds, e.g., potassium titanyl phosphate,  $\text{K}(\text{TiO})\text{PO}_4$ .

The addition of soluble sulfides to titanium solutions results in the precipitation of the dioxide, but the **sulfide** may be formed by heating chloride and hydrogen sulfide vapors together:  $\text{TiCl}_4 + 2\text{H}_2\text{S} = \text{TiS}_2 + 4\text{HCl}$ . The sulfide does not form polysulfides with alkali sulfides. At high temperatures, the element unites with sulfur, forming  $\text{TiS}$  and  $\text{Ti}_2\text{S}_3$ .

### ZIRCONIUM COMPOUNDS

11. Zirconium forms the **dioxide** and possibly two oxides of lower oxidation states, but the evidence in favor of these is of doubtful nature. The dioxide occurs in nature as the mineral baddeleyite. Like titania, it reacts with fused hydroxides and carbonates, forming insoluble **zirconates**, e.g.,

$\text{Na}_2\text{ZrO}_3$ ,  $\text{CaZrO}_3$ ,  $\text{PbZrO}_3$ . The oxide is widely used in ceramics as a constituent of enamels. The hydrated oxide, usually regarded as **zirconium hydroxide**,  $\text{Zr}(\text{OH})_4$ , is formed as a **hydrogel** upon the addition of alkali to solutions of zirconium salts. The hydroxide is readily soluble in acids and somewhat soluble in cold concentrated alkali, with which it reacts mainly to form insoluble zirconate. Hydrogen peroxide reacts with the hydroxide to form the **hydrated peroxide**, probably  $\text{H}_4\text{ZrO}_5$ . In sulfuric acid solution the complex peroxysulfate,  $\text{O}_2\text{ZrO}_2\text{SO}_4\text{ZrO}_2$ , appears to be formed.

The **tetrahalides** resemble those of titanium in properties and methods of formation. Basic halides are obtained upon evaporation of the water solutions of the halides, e.g., **zirconyl chloride**,  $\text{ZrOCl}_2$ . The latter is employed in tanning. Many slightly soluble **fluorozirconates** are known, e.g.,  $\text{K}_2\text{ZrF}_6$ ,  $\text{BaZrF}_6$ , and also less stable **chlorozirconates**.

Reduction of the tetrachloride with aluminum at  $300^\circ$  yields the **trichloride**,  $\text{ZrCl}_3$ , and at higher temperatures, the **dichloride**,  $\text{ZrCl}_2$ , but these compounds cannot be formed in water solutions.

**Zirconium sulfides, sulfates, nitrates, and phosphates** resemble closely the corresponding titanic compounds. The normal sulfate may be crystallized from concentrated sulfuric acid solutions, and many basic and double sulfates are known. Hydrogen reacts with zirconium at red heat, apparently forming the unstable **hydride**,  $\text{ZrH}_2$ .

The naturally occurring **silicate**,  $\text{ZrSiO}_4$ , known as **zircon** or **jargon**, is valued as a jewel. On account of their luster and hardness (7.5) zircons are employed as substitutes for diamonds. They occur in a great variety of colors, red, green, blue, and white.

## HAFNIUM COMPOUNDS

**12.** Hafnium resembles zirconium so closely that the presence of several per cent of hafnium in the zirconium



compounds was not discovered until 1923, although the chemistry of zirconium was carefully investigated during the preceding century. Any compound formed by the one element appears to be formed by the other, and, as a rule, the melting points, boiling points, and solubilities of the two compounds are very similar. Hafnium dioxide and hydroxide appear to be slightly more basic than the zirconium compounds.

### THORIUM COMPOUNDS

**13. Thorium dioxide**, or **thoria**, appears to possess no acid properties, even when fused with alkali, and in this respect differs from the other members of the group. The unhydrated oxide dissolves but slowly in acids, but the hydrated form,  $\text{ThO}_2 \cdot 2\text{H}_2\text{O}$ , or **thorium hydroxide**,  $\text{Th}(\text{OH})_4$ , is readily soluble in acids. The hydroxide is formed as a gelatinous precipitate upon the addition of alkali hydroxides or ammonia to thorium salts in solution. Lower oxides have not been prepared, but a hydrated **peroxide** is formed by the action of hydrogen peroxide upon solutions of thorium salts; the formula appears to be,  $\text{Th}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ .

Mixtures of thorium and cerium dioxides, heated to a high temperature, exhibit a brilliant white luminescence, the maximum emissivity being obtained with about 1 per cent of cerium dioxide. Advantage is taken of this fact in the **Welsbach gas mantles**, which are manufactured by saturating fabric with the nitrates of these metals. When ignited, the oxide residue retains the shape of the original fabric. A few per cent of beryllium and magnesium nitrates are usually added to give the ash greater strength. The dioxide is employed in the manufacture of laboratory crucibles to stand temperatures as high as  $2300^\circ \text{C}$ .

The **tetrahalides** are prepared by methods characteristic of the group. The **fluoride**,  $\text{ThF}_4$ , and its hydrate,  $\text{ThF}_4 \cdot 4\text{H}_2\text{O}$ , are very slightly soluble, as is also the **potassium fluorothorate**,  $\text{K}_2\text{ThF}_6 \cdot 4\text{H}_2\text{O}$ . Various hydrates of the

**tetrachloride** may be crystallized from aqueous solution, providing sufficient acid is present to prevent the precipitation of **basic chlorides**. Lower valent halides have not been prepared. The **sulfide** may be made by the action of sulfur or hydrogen sulfide upon the heated metal. It is not stable in water solutions. The anhydrous **sulfate** is very hygroscopic and forms hydrates containing 9, 8, 6, 4, and 2 moles of water. The **nitrate**,  $\text{Th}(\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$ , may be crystallized from concentrated acid solutions, and the phosphate,  $\text{Th}_3(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ , is formed as a gelatinous precipitate by adding sodium phosphate to a solution of a thorium salt. Both the nitrate and phosphate form many double salts, e.g.,  $\text{KTh}(\text{NO}_3)_5 \cdot 9\text{H}_2\text{O}$ , and  $\text{NaTh}_2(\text{PO}_4)_3$ . Normal thorium carbonate has not been prepared, but a number of **basic carbonates** and **complex carbonates** are known, e.g.,  $\text{ThO} \cdot \text{CO}_3 \cdot 2\text{H}_2\text{O}$ , and  $(\text{NH}_4)_2\text{Th}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ . The basic carbonates are soluble in excess ammonium carbonate, probably with the formation of complex carbonate. The **iodate**,  $\text{Th}(\text{IO}_3)_4$ , is but slightly soluble and resembles the corresponding ceric compound.

**14. Analytical.**—Titanium may be extracted from its ores by alkaline fusion, followed by digestion in acid, or by fusion with potassium acid sulfate and extraction with water. The addition of hydrogen peroxide to a sulfuric acid solution of titanium produces the characteristic yellow or orange color of the peroxy-acid. Titanic solutions may be reduced to the violet + 3 state by zinc in hot acid solution, and the titanium may be determined quantitatively by titrating this solution with permanganate. Titanium hydroxide is precipitated by the addition of alkalies, ammonia, and soluble carbonates and sulfides to solutions of titanium salts. If formed in cold solution, it is readily soluble in acids, and somewhat soluble in excess alkali. Precipitated from hot solution, it is not rapidly soluble in acid.

Zirconium and hafnium ores may be got into solution by methods similar to those given for titanium. The two ele-

ments may be separated from iron, aluminum, beryllium, titanium, and thorium by precipitation from highly acid solutions, as the very slightly soluble zirconyl and hafnyl phosphates,  $\text{ZrO}(\text{H}_2\text{PO}_4)_2$ . Alkalies precipitate zirconium and hafnium hydroxides, which are not soluble in excess of the reagent. Ammonium oxalate or oxalic acid precipitate the oxalates, soluble in excess of the reagents. Separation from iron may be accomplished through the slight solubility of the potassium complex fluorides.

Hafnium and zirconium are extremely difficult to separate from each other. The greatest difference in the solubilities of their compounds appears to exist in the citrates, the hafnium salt being the more soluble. Separation may also be carried out through the fractional precipitation of the phosphates, oxychlorides, and the ammonium and potassium complex fluorides. The per cent of hafnia and zirconia in a sample may be estimated by determination of the density of the oxide mixture. The values for the pure oxides are  $\text{ZrO}_2$ , 5.73, and  $\text{HfO}_2$ , 9.68.

Thorium is readily extracted from its ores by digestion with hydrochloric or sulfuric acids. Ammonia and the alkalies precipitate the hydroxide, which is not soluble in excess of the reagent. Thorium and cerium are separated from the rare earths through the very slight solubilities of the iodates,  $\text{Th}(\text{IO}_3)_4$  and  $\text{Ce}(\text{IO}_3)_4$ , even in rather concentrated acid. Other slightly soluble compounds are:  $\text{K}_4\text{Th}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{ThO} \cdot \text{CO}_3 \cdot 8\text{H}_2\text{O}$ ,  $\text{K}_2\text{ThF}_6 \cdot 4\text{H}_2\text{O}$ ,  $\text{Th}(\text{C}_2\text{O}_4)_2$ ,  $\text{Th}_3(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ , and  $\text{ThFe}(\text{CN})_6$ .

## GERMANIUM, TIN, AND LEAD

**15. Occurrence.**—The elements of this group constitute but a very small portion of the igneous rocks, the estimated percentages being germanium,  $10^{-11}$ , tin,  $10^{-6}$ , and lead,  $2 \times 10^{-5}$ . They do, however, occur frequently in workable deposits.

Germanium is found in many sulfide ores, especially those of silver, lead, tin, antimony, and zinc. In a number of ores definite sulfide complexes appear to be present, such as  $\text{Ag}_4\text{GeS}_4$  and  $\text{Pb}_2\text{GeS}_4$ . An English coal ash has been reported which contains 1.6 per cent  $\text{GeO}_2$ .

The most important tin mineral is the oxide,  $\text{SnO}_2$ , called **cassiterite**. Deposits of cassiterite in Cornwall, England, were worked as early as 1000 B.C. by the Phoenicians. The principal sources of the metal at present are mines in the Malay States, Bolivia, and the Dutch East Indies. Tin also occurs as complex sulfides, e.g.,  $\text{SnCu}_2\cdot\text{FeS}_4$ ,  $\text{Pb}_5\text{Sn}_2\cdot\text{Sb}_2\text{S}_{12}$ , and  $\text{Ag}_8\text{SnS}_6$ , and as complex oxides, e.g.,  $\text{CaSnO}_4(\text{BO})_2$  and  $\text{CaO}\cdot\text{SnO}_2\cdot 3\text{SiO}_2\cdot 2\text{H}_2\text{O}$ , but these minerals are of slight importance.

The principal lead ore is the sulfide or **galena**,  $\text{PbS}$ , and this is generally associated with sulfides of silver, copper, arsenic, antimony, bismuth, and tin. Other common ores are **cerussite**,  $\text{PbCO}_3$ , and **anglesite**,  $\text{PbSO}_4$ , which appear to have been formed by the weathering of sulfide ores. Complex oxides and oxychlorides of the metals of Groups V and VI also occur.

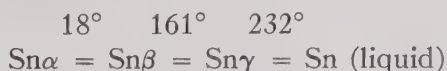
TABLE III  
ATOMIC AND PHYSICAL PROPERTIES OF GERMANIUM, TIN, AND LEAD

	GE	SN	PB
Atomic weight.....	72.60	118.70	207.22
Atomic number.....	32	50	82
Isotopes.....	70, 72, 73, 74, 76	112, 114, 115, 116, 117, 118, 119, 120, 122, 124	204, 206, 207, 208
Melting point, °C.....	958	231.8	327.5
Boiling point, °C.....	2700	2260	1620
Density, g/c.....	5.36	W 7.31 G 5.75	11.34
Electrical resistivity, ohm-cm. at 20° C.....	$89 \times 10^{-3}$	$11.4 \times 10^{-6}$	$21.9 \times 10^{-8}$
Size of $\text{M}^{+4}$ ion in crystal, cm. $\times 10^8$ (if $\text{Cl}^- = 1.81$ ).....	0.53	0.71	0.84
Ionization Potentials,			
1st electron.....	8.09	7.30	7.38
2d electron.....	15.86	ca 14.5	14.96

**16. Metallic Germanium.**—The metal may be prepared by reduction of the dioxide with carbon at red heat, or by the reduction of the oxide or sulfide by heating with potassium cyanide. Germanium is a greyish-white metal, rather hard and brittle. It forms good tarnish resisting mirrors. X-ray data for the solid indicate that the atoms are arranged in a modified diamond structure. The metal is not a good electrical conductor.

**17. Tin.**—Cassiterite is easily reduced to the metal by smelting with carbon in a reverberatory furnace:  $\text{SnO}_2 + \text{C} = \text{Sn} + \text{CO}_2$ . The liquid metal is drawn off from the furnace and cast into molds. The greatest difficulty in the metallurgy is the purification of the ore before smelting. This is carried out by roasting, to remove sulfur and arsenic, and if tungsten is present, the ore is fused with sodium carbonate and the tungsten extracted with water. The crude metal usually contains some compounds of iron and arsenic, which may be removed by carefully melting the ingots (liquation), as the compounds melt at temperatures somewhat higher than the pure metal. The annual production of tin is about 170,000 tons.

Tin exists in three solid forms, with definite transitions as summarized in the following scheme:



The  $\beta$ -form is the ordinary white tin. The transition of white tin to  $\alpha$  or grey tin is slow at the transition temperature, but at  $-50^\circ$  the transformation is complete in a few days if a little of the latter form is present to start the reaction. The transition is accompanied by an increase in volume, and the product is a brittle substance which is readily powdered. The phenomenon was first observed in cold countries in the disintegration of organ pipes and other tin objects, and was called "**tin disease.**" Grey tin is cubic, with the diamond lattice structure, while white



tin is tetragonal with a ditetragonal-bipyramidal lattice.  $\Gamma$ -Tin belongs to the rhombic system.

White tin is very malleable, and may be rolled into thin sheets called tinfoil, which is used extensively for wrapping. It is very resistant to corrosion, whence its use in tinning iron and copper surfaces. Tin does not, however, give the galvanic protection afforded by zinc (cf. VII—4), since tin is not a more powerful reducing agent than iron. Tin forms many useful alloys. (See Table IV and also Copper and Bismuth.)

**18. Lead.**—The metallurgy of lead is concerned largely with the reduction of the sulfide, and this may be brought about in several ways. (1) Part of the sulfide may be roasted to the oxide,  $\text{PbO}$ , or sulfate,  $\text{PbSO}_4$ , and the oxidized ore heated with more of the sulfide:  $2\text{PbO} + \text{PbS} = 3\text{Pb} + \text{SO}_2$ ; and  $\text{PbSO}_4 + \text{PbS} = 2\text{Pb} + 2\text{SO}_2$ . (2) The ore may be roasted to the oxide and this reduced with carbon or carbon monoxide:  $\text{PbO} + \text{CO} = \text{Pb} + \text{CO}_2$ . (3) The

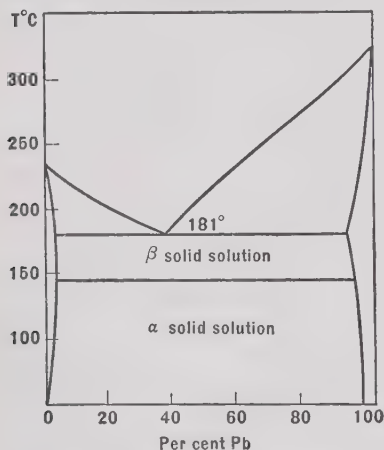


FIG. 1. Lead-tin temperature-composition curves.

sulfide may be reduced by heating with scrap iron:  $\text{PbS} + \text{Fe} = \text{Pb} + \text{FeS}$ . The iron may be added as such, or it may be produced in the furnace from a mixture of iron oxides and carbon. In the United States, the ore is generally first concentrated by "flotation" (cf. VII—5), and the smelting process is a combination of the three methods outlined above. A mixture of part roasted and part unroasted ore with iron

oxide and carbon is heated in a blast furnace. Copper present collects in the iron sulfide matte, while silver and gold dissolve in the molten lead. In the refinement



of the crude blast furnace lead, the more electropositive impurities are generally removed by melting the metal and keeping it molten for several hours with frequent stirring. The impurities, when oxidized, rise to the surface and are skimmed off. Some lead, especially if high in bismuth, is now refined electrolytically, using as an electrolyte a solution of lead fluosilicate. The crude lead serves as the anode, and a bag about the anode collects the "mud" from which bismuth and the noble metals are recovered. The annual production of lead is about 1,500,000 tons, of which about one fourth is produced in the United States.

Ordinary lead is very largely a mixture of the two isotopes, 208 and 206. Lead extracted from uranium ores is largely the lower isotope, and has a density of 11.27 as compared with 11.34 for ordinary lead. The crystal lattice of the metal is of the face centered type. The metal is so soft that it can be squirted, under pressure, into pipes and even into fine wire or rolled into thin sheets, but it lacks tensile strength. Lead may be hardened by the addition of antimony or the alkaline earth metals. The most important industrial uses of lead are in the manufacture of storage batteries, preparation of white lead and other pigments, manufacture of cable coverings, in plumbing, and in acid works. Important alloys of lead are listed in Table IV.

TABLE IV  
ALLOYS OF TIN AND LEAD

Britannia	Sn 90, Sb 10	Hard metal, Pb 90, Sb 10
Babbitt	Sn 90, Sb 7, Cu 3	Frary metal, Pb 90, Ca 10
Antifriction	Sn 75, Sb 12.5, Cu 17.5	Type metal, Pb 82, Sb 15, Sn 3
Solder	Sn 50, Pb 50	White metal, Pb 75, Sb 14, Sn 10, Cu 1
Pewter	Sn 80, Pb 20	Rose metal, Bi 50, Pb 27.1, Sn 22.9
Aluminum		Battery plate, Pb 94, Sb 6
solder	Sn 86, Zn 9, Al 5	

**19. Reactions of the Metals.**—The metals are powerful reducing agents in the presence of an alkaline solution and

fairly strong in acid solutions. Pure tin and lead do not evolve hydrogen readily with acids due to high over-voltage effects (Append. I). Lead is quite resistant to the action of even moderately concentrated sulfuric acid, but is readily oxidized by oxygen in the presence of various weak organic acids, e.g. acetic acid.

TABLE V  
REACTIONS OF Ge, Sn, AND Pb

$M + O_2 = MO_2$	Lead forms $PbO$ or $Pb_3O_4$
$M + 2H^+ = M^{++} + H_2$	Not with Ge. Slowly with Sn and Pb
$M + 2S = MS_2$	Lead forms only $PbS$
$M + 2X_2 = MX_4$	With halogens, except $PbI_4$
$M + 2OH^- = MO_2^{--} + H_2$	Slowly with Sn and Pb. Ge forms $GeO_3^{--}$
$M = M^{++} + 2e^-$	Ge <i>ca.</i> 0.25, Sn 0.14, Pb 0.13 (values in volts)
$3Ge + 4HNO_3 = 3GeO_2 + 4NO + 2H_2O$	
$3Sn + 4HNO_3 = 3SnO_2 + 4NO + 2H_2O$	Forms slightly soluble metastannic acid
$3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O$	
$Pb + 2CH_3CO_2H + \frac{1}{2}O_2 = Pb(CH_3CO_2)_2 + H_2O$	Also with other acids
$Pb + 2H_2O + O_2 = Pb(OH)_2 + H_2O_2$	Slowly at moderate temperatures

## GERMANIUM COMPOUNDS

**20. Germanium dioxide**,  $GeO_2$ , is readily formed by roasting the sulfide minerals. The oxide is not soluble in nitric or sulfuric acids, but is dissolved when heated with concentrated hydrofluoric or hydrochloric acids with the formation of volatile **tetrahalides**. The halides are hydrolyzed in water with the precipitation of the hydrated dioxide, except the fluoride, which forms a mixture of the dioxide and **fluogermanic** acid,  $H_2GeF_6$ . The potassium salt,  $K_2GeF_6$ , is but slightly soluble. The dioxide is soluble in alkalis forming **germanates**, e.g.  $Na_2GeO_3$ .

Germanium **disulfide**,  $GeS_2$ , may be precipitated in strong sulfuric acid by hydrogen sulfide, but yields a colloidal

suspension in dilute acid. It is soluble in alkali sulfide, forming **thiogermanates**.

Germanium resembles silicon in the formation of an unstable **hydride**,  $\text{GeH}_4$ , and also traces of the heavier compounds,  $\text{Ge}_2\text{H}_6$  and  $\text{Ge}_3\text{H}_8$ , when germanium compounds are reduced with aluminum in alkaline solution. The metal heated in a stream of hydrogen chloride forms **germanium chloroform**,  $\text{GeHCl}_3$ . This compound hydrolyzes to form **germanous acid**, which appears to resemble formic acid in structure:  $\text{GeHCl}_3 + 2\text{H}_2\text{O} = 3\text{HCl} + \text{HGeO}(\text{OH})$ . The acid is soluble in alkalis, forming **germanites**, and upon heating forms **germanous oxide**,  $\text{GeO}$ , which possesses basic properties in that it is soluble in acids. **Germanous halides** and the **sulfides** may be prepared by igniting strongly the + 4 compounds, e.g.  $\text{GeI}_4 = \text{GeI}_2 + \text{I}_2$ . The germanous ion is readily oxidized,  $2\text{H}_2\text{O} + \text{Ge}^{++} = \text{GeO}_2 + 4\text{H}^+ + 2e^-$ , *ca.* 0.2 volt. Germanite ion is said to be unstable with respect to its own oxidation and reduction. The compound  $(\text{GeOOH})_2$  analogous to oxalic acid is known. The reaction of  $\text{CaGe}$  with  $\text{HCl}$  produces polymers of  $\text{GeH}_2$ .

### COMPOUNDS OF TIN

**21. Oxidation States.**—The stability of the two oxidation states of tin in respect to oxidizing and reducing agents is indicated by the following potentials:

	VOLTS
$\text{Sn} = \text{Sn}^{++} + 2e^-$ .....	+ 0.13
$\text{Sn}^{++} = \text{Sn}^{++++} + 2e^-$ .....	- 0.13
$3\text{OH}^- + \text{Sn} = \text{HSnO}_2^- + \text{H}_2\text{O} + 2e^-$ .....	- 0.79
$\text{H}_2\text{O} + 3\text{OH}^- + \text{HSnO}_2^- = \text{Sn}(\text{OH})_6^{--} + 2e^-$ .....	0.96

It follows from these values that the equilibrium,  $\text{Sn} + \text{Sn}^{++++} = 2\text{Sn}^{++}$ , favors the reaction as written, that is, soluble stannic compounds may be reduced to stannous by the metal. The equilibrium is reversed in alkaline solutions:  $2\text{H}_2\text{O} + 2\text{HSnO}_2^- = \text{Sn} + \text{Sn}(\text{OH})_6^{--}$ .

**22. Oxides and Hydroxides.**—The **dioxide**,  $\text{SnO}_2$ , is the principal tin ore. The crystal lattice is similar to rutile. When fused with alkalis, the oxide forms **stannates**, e.g.,  $\text{Na}_2\text{SnO}_3$ . The alkali stannates are soluble in water, and upon the addition of acid to the solution precipitate “ $\alpha$ -stannic acid” or  $\alpha$ -hydrous oxide. This acid or hydrous oxide is amphoteric, and readily dissolves in excess of either base or acid.

Another hydrous oxide,  $\beta$ -oxide (also called metastannic acid) is formed by the action of nitric acid upon tin or by the hydrolysis of stannic salts in hot solutions. This compound is not soluble in excess of any acid, but is peptized by concentrated hydrochloric acid to form a sol which may be dissolved in dilute acid. The composition of the two “acids” appears to be the same, the different behavior being due to differences in physical state. X-ray diffraction patterns of both are identical with cassiterite. Sodium hydroxide dissolves the  $\beta$ -oxide.

**23. Stannous oxide**,  $\text{SnO}$ , may be prepared by heating stannous hydroxide or oxalate, or by heating the metal in a limited supply of oxygen. It burns when heated in air to form the dioxide. Hydrous hydrated stannous oxide, probably  $\text{SnO} \cdot \frac{1}{2}\text{H}_2\text{O}$ , is precipitated by the addition of alkalis to stannous solutions. It is also amphoteric, dissolving in alkali hydroxides, but not in ammonia or soluble carbonates. Solutions of **stannites** are powerful reducing agents.

**24. Peroxystannic acids**,  $\text{H}_2\text{Sn}_2\text{O}_7$  and  $\text{HSnO}_4$ , and their salts, are formed by the action of peroxides on stannic solutions, or by the anodic oxidation of cold solutions of alkali stannates.

**25. Halides.**—The anhydrous **stannic halides** may be prepared by the action of the halogens on the metal and aqueous solutions of the salts by dissolving stannic oxide in the hydrohalic acid. Complex halidostannates are formed in solution and a number of these soluble salts may

be obtained upon crystallization, e.g.,  $K_2SnF_6$ . **Stannic chloride** is important commercially as a mordanting agent. It crystallizes from an acid solution as  $SnCl_4 \cdot 5H_2O$  although the anhydrous compound is a liquid. The **ammonium chlorostannate**,  $(NH_4)_2SnCl_6$ , is also used in dyeing under the name "pink salt."

**Stannous halides** are readily prepared from the stannic by reduction with tin, or by dissolving the metal in the halogen acid. The solutions are readily oxidized by air. **Stannous chloride** is also important as a mordant. The salt is very soluble in water, but forms the basic salt,  $Sn(OH)Cl$ , unless acid is present to prevent hydrolysis.

**26. Sulfides.**—**Stannous** and **stannic sulfides** may be prepared by fusing the elements together, but the latter is unstable at high temperatures:  $SnS_2 = SnS + S$ . Hydrogen sulfide precipitates brown stannous and yellow stannic sulfide from dilute acid solutions of stannous and stannic salts respectively. Both sulfides are soluble in concentrated hydrochloric acid but stannic sulfide, being the more acid in nature, is the less soluble of the two. The disulfide is amphoteric and dissolves in excess of sulfide to form **thiostannates**:  $SnS_2 + S^{--} = SnS_3^{--}$ . The stannous sulfide is not soluble in excess sulfide unless polysulfide is present, in which case it is oxidized to thiostannate:  $SnS + S_2^{--} = SnS_3^{--}$ . The thiostannates are not stable in acid solution:  $SnS_3^{--} + 2H^+ = H_2SnS_3 = H_2S + SnS_2$ .

Stannic sulfide has long been used as a gilding pigment under the name of **mosaic gold**. The preparation is carried out by heating together a mixture of tin, sulfur, ammonium chloride, and mercury. The exact action of the two latter substances is uncertain, but they volatilize and leave the sulfide as brilliant yellow crystals.

**27. Other Tin Compounds.**—Small amounts of the **hydride**,  $SnH_4$ , are formed by the cathodic reduction of tin in dilute acid solution, and by the action of acid upon tin-magnesium alloy. Both stannous and stannic **carbon-**

ates are completely hydrolyzed to the hydroxides. Both of the **nitrates** and the **sulfates** are formed in solution by the action of the acids upon the hydroxides, but they are difficult to crystallize without the formation of basic salts. Slightly soluble **stannous phosphate**,  $\text{Sn}_5\text{H}_2(\text{PO}_4)_4 \cdot 3\text{H}_2\text{O}$ , may be precipitated from slightly acid stannous chloride by sodium acid phosphate, and a number of slightly soluble basic and double stannic phosphates are known.

### LEAD COMPOUNDS

**28. Oxidation States.**—The most important oxidation reduction potentials for lead are given below:

	VOLTS
$\text{Pb} = \text{Pb}^{++} + 2e^-$ .....	+ 0.126
$\text{Pb} + \text{SO}_4^{--} = \text{PbSO}_4 + 2e^-$ .....	+ 0.355
$\text{Pb} + 3\text{OH}^- = \text{HPbO}_2^- + \text{H}_2\text{O} + 2e^-$ .....	+ 0.54
$\text{Pb}^{++} + 2\text{H}_2\text{O} = \text{PbO}_2 + 4\text{H}^+ + 2e^-$ .....	- 1.456
$\text{PbSO}_4 + 2\text{H}_2\text{O} = \text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{--} + 2e^-$ .....	- 1.685
$\text{PbO} + 2\text{OH}^- = \text{PbO}_2 + \text{H}_2\text{O} + 2e^-$ .....	- 0.25

It follows that lead is a fair reducing agent in acid solutions, and a strong reducing agent in alkaline solutions, and that the dioxide is an extremely powerful oxidizing agent in acid solutions but much weaker in alkaline solutions.

**29. Oxides and Hydroxides.**—Lead forms the **monoxide**,  $\text{PbO}$ , and the **dioxide**,  $\text{PbO}_2$ . Two additional oxides appear to be plumbous plumbate salts, the **trioxide**,  $\text{Pb}_2\text{O}_3$  being  $\text{PbPbO}_3$ , and **red lead**,  $\text{Pb}_3\text{O}_4$ , being  $\text{Pb}_2\text{PbO}_4$ . The existence of a so-called suboxide or its salts is extremely doubtful.

The monoxide, or **litharge**, orange-yellow, is prepared by heating the metal in air; and around  $550^\circ \text{C}$ . the other oxides evolve oxygen to form the monoxide. The oxide is soluble in acids and alkalis, forming respectively **plumbous**,  $\text{Pb}^{++}$ , and **plumbite**,  $\text{HPbO}_2^-$ , ions, and the addition of alkalis, and acid, respectively, to these solutions, precipitates the "hydroxide," or hydrous hydrated oxide, possibly  $\text{PbO} \cdot \frac{1}{2}\text{H}_2\text{O}$ , which is soluble in excess of either reagent. The



“hydroxide” is more basic than stannous “hydroxide” as is indicated by the formation of a carbonate.

Litharge is used in glazing pottery and in making glass. A mixture with glycerine is sometimes used as a cement, since it sets to a solid lead glyceride.

**Red lead** or **minium** is made by carefully heating the monoxide at temperatures below  $500^{\circ}$ . The composition of the product varies with the temperature of roasting, a maximum of  $\text{PbO}_2$  (33 per cent) is obtained at about  $430^{\circ}$ . When treated with nitric acid, it is decomposed:  $\text{Pb}_3\text{O}_4 + 4\text{HNO}_3 = 2\text{Pb}(\text{NO}_3)_2 + \text{PbO}_2 + 2\text{H}_2\text{O}$ . Red lead is used in making flint glass, and as a red pigment. Structural iron is often given a first coat of red lead paint as it serves very effectively to protect the iron from corrosion, due possibly to the iron becoming passive.

**30. Lead dioxide** may be prepared from red lead as indicated above, but it is most readily formed by the oxidation of lead monoxide or plumbites in dilute alkali solutions, e.g.,  $\text{PbO} + \text{ClO}^- = \text{PbO}_2 + \text{Cl}^-$ . The oxide is also readily prepared by the anodic oxidation of solutions of plumbous ion. The dioxide has the rutile type of crystal lattice, and is a fair electrical conductor. It is only slightly soluble in water and is comparatively inert toward hydrogen and hydroxide ions. Concentrated alkalies do, however, dissolve the oxide forming **plumbates**, and soluble metaplumbates may be formed by fusing the oxide with alkalies. Many plumbates, both ortho and meta, of the more basic + 2 oxides have also been prepared. The oxide is slowly soluble in dilute nitric acid, but the tetravalent lead ion oxidizes water with the evolution of oxygen. Cold concentrated hydrochloric acid forms liquid tetrachloride, but at ordinary temperatures chlorine is evolved. For the use of the dioxide in the lead storage battery, see Paragraph 39.

**31. Lead Halides.**—Lead **tetrafluoride** is formed upon heating the dioxide with potassium acid fluoride, although

the product does not appear to be the pure compound. The formation of the **tetrachloride** is discussed in the preceding paragraph. In dilute acid, both halides are hydrolyzed to the dioxide; in the concentrated halogen acids, the **fluoplumbic acid**,  $\text{H}_2\text{PbF}_6$ , and **chloroplumbic acid**,  $\text{H}_2\text{PbCl}_6$ , are formed. Alkali salts of both of these acids have been prepared.

The plumbous halides are but sparingly soluble in cold water, but the chloride and bromide are readily soluble in hot water, and the iodide partially soluble. The solubility of the halide is decreased in dilute solutions containing the halogen ion but is increased in concentrated solutions, doubtless with the formation of complex ions, such as  $\text{PbCl}_4^{--}$ .

**32. Nitrate.**—The nitrate,  $\text{Pb}(\text{NO}_3)_2$ , is readily soluble, but unless a slight excess of acid is present to prevent hydrolysis, basic nitrates are precipitated.

**33. Acetate.**—The acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , called **sugar of lead**, is one of the few soluble lead salts, and it appears to form a complex ion with excess acetate. Like the nitrate, the solution tends to form basic salts, but the basic compound,  $\text{Pb}(\text{OH})\text{C}_2\text{H}_3\text{O}_2$ , is soluble. Both the acetate and nitrate are extremely poisonous.

The dioxide is soluble in glacial acetic acid with the formation of the tetra-acetate, but this compound is completely hydrolyzed in water.

**34. Sulfate.**—The sulfate,  $\text{PbSO}_4$ , resembles the alkaline earth sulfates in being slightly soluble in water. It is soluble in excess acetate (see above), and in excess alkali it dissolves to form plumbite. The basic sulfate,  $\text{Pb}_2\text{OSO}_4$ , known as the pigment "sublimed white lead," is made by roasting lead sulfide with carbon. The product sublimes and is condensed to a pure white powder. The commercial pigment usually contains excess of  $\text{PbSO}_4$  and some zinc oxide.

**35. Chromate.**—The chromate,  $\text{PbCrO}_4$ , is very slightly soluble in water, but dissolves readily in acids with the

formation of dichromate, and in bases with the formation of plumbite. It is an important yellow pigment, **chrome-yellow**. The stable yellow modification of lead chromate is monoclinic. A red tetragonal modification may be stabilized by the addition of lead molybdate. This pigment is known as **molybdenum orange**.

**36. Sulfide.**—The occurrence of the sulfide in the mineral galena and its metallurgy has been discussed. The sulfide is precipitated from dilute acid solutions by hydrogen sulfide, but is soluble in concentrated hydrochloric acid and in hot 2*N* nitric acid. It is not soluble in excess sulfide. The crystal has the sodium chloride type of lattice. It acts as a rectifier for oscillating electric currents.

**37. Lead Carbonate.**—Normal lead carbonate,  $\text{PbCO}_3$ , may be prepared by the action of sodium bicarbonate solution upon lead chloride or sulfate. When soluble carbonates are added to a solution of lead ion, the **basic carbonate**,  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ , is formed. This compound is extremely important as the pigment **white lead**. The annual consumption in the United States is about 100,000 tons. It is prepared commercially by the action of air, carbon dioxide, and acetic acid upon the metal. A small amount of acetic acid serves to convert a large quantity of lead into the carbonate. The following reactions may represent the mechanism of the process:  $2\text{Pb} + \text{O}_2 + 2\text{HAc} = 2\text{Pb}(\text{OH})\text{Ac}$ ;  $6\text{Pb}(\text{OH})\text{Ac} + 2\text{CO}_2 = \text{Pb}_3(\text{OH})_2(\text{CO}_3)_2 + 3\text{PbAc}_2 + 2\text{H}_2\text{O}$ ; and  $2\text{Pb} + \text{O}_2 + 2\text{PbAc}_2 + 2\text{H}_2\text{O} = 4\text{Pb}(\text{OH})\text{Ac}$ . In the older forms of the process, perforated lead disks were placed over pots containing acetic acid. Tiers of these pots were stacked with tan bark which decomposed under bacterial action, liberating carbon dioxide and also providing heat. This process required about three months for completion, and more rapid methods are now being used to some extent, as for example, the churning of lead dust with acetic acid, air, and carbon dioxide.

The covering power of white lead is excellent, but it has

the disadvantage of darkening due to the formation of the sulfide, and its poisonous nature is also objectional.

**38. Other Lead Compounds.**—Lead **orthophosphate**,  $\text{Pb}_3(\text{PO}_4)_2$ , may be precipitated from dilute acid plumbous solutions by disodium phosphate. Many basic and double phosphates are also known. Lead **silicate**,  $\text{PbSiO}_3$ , is formed by fusing lead monoxide and silica. It is a constituent of lead glass and of certain glazes used on earthenware.

**39. Lead Storage Battery.**—The ordinary lead accumulator depends upon the reversibility of the reaction:  $\text{Pb} + \text{PbO}_2 + 4\text{H}^+ + 2\text{SO}_4^{--} = 2\text{PbSO}_4 + 2\text{H}_2\text{O}$ . When fully charged, one electrode consists of a plate of spongy lead, the other electrode a plate impregnated with lead dioxide, and the electrolyte is sulfuric acid. The half reactions for discharge are:  $\text{Pb} + \text{SO}_4^{--} = \text{PbSO}_4 + 2e^-$  and  $\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{--} + 2e^- = \text{PbSO}_4 + 2\text{H}_2\text{O}$ . Lead sulfate

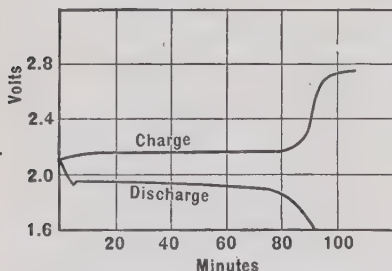


FIG. 2. Charge and discharge curves for the lead storage battery at 15°C.

thus forms on each plate upon discharge, and the concentration of sulfuric acid decreases. The density of the acid under normal conditions is 1.20 at 2.05 volts (charged) and 1.05 at 1.91 volts (discharged). The cell is not completely reversible as is evident from the higher voltage required to reverse

the reaction and recharge the cell (Fig. 2). The final rapid increase in the charging voltage curve occurs when all the solid sulfate is used up and the concentration of the lead ion diminishes.

**40. Analytical.**—Advantage is taken of the slight solubility of the sulfides of the group in qualitative analysis. The reactions of these compounds with acids and bases have been discussed, and reference should be made to

Appendix VI for the treatment of tin and lead in the systematic separation of the positive ions. The reduction of mercuric chloride, first to mercurous and then to grey metallic mercury by stannous ion, is used as a confirmatory test for tin, and the slight solubilities of  $\text{PbSO}_4$  and  $\text{PbCrO}_4$  are used in the confirmation of lead.

Germanium is determined quantitatively by precipitating as the disulfide and weighing as the dioxide.

Tin is sometimes determined gravimetrically as the dioxide, but it is most readily determined by the volumetric titration of stannous ion by iodine:  $\text{Sn}^{++} + \text{I}_3^- = \text{Sn}^{++++} + 3\text{I}^-$ . The reduction of any stannic salts prior to the titration is accomplished with aluminum foil in acid solution, or by nickel in hydrochloric acid.

In gravimetric analyses, lead is often precipitated and weighed as the sulfate,  $\text{PbSO}_4$ , chromate,  $\text{PbCrO}_4$ , or molybdate,  $\text{PbMoO}_4$ . In the precipitation as the sulfate, separation from barium is secured by dissolving out the lead in ammonium acetate and dilute sulfuric acid, and reprecipitating. The molybdate method has the advantage that the barium salt is soluble.

Lead is often determined electrolytically by anodic precipitation as the dioxide from a nitric acid solution, using a large platinum anode.

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# Chapter XVI

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## SUBGROUP V. VANADIUM, COLUMBIUM, TANTALUM

1. The elements of Subgroup V occur in transition series resulting from the building up of the number of electrons in the outer shell of the kernel from eight to eighteen (Append. XVIII). Spectral data indicate that the normal gaseous atoms have two electrons in the outer *s* orbital, so that three additional valence electrons must, in the normal atom, be located in lower *d* orbitals. However, all five valence electrons are removable, and all members of the group form compounds of the + 5 oxidation state.

The elements are semi-noble, steel-like metals with high melting points. Vanadium forms compounds of all its possible positive oxidation states except + 1. Unlike the main Group V, the + 5 state becomes more stable with increasing atomic weight; and the pentoxide, which is amphoteric in the case of vanadium, becomes more inert to the action of both acids and bases.

2. **Occurrence.**—Vanadium is estimated as present in igneous rocks to the extent of  $1.7 \times 10^{-4}$  per cent, and columbium and tantalum together as  $3 \times 10^{-5}$  per cent.

The principal vanadium minerals are **vanadinite**,  $\text{Pb}_2(\text{VO}_4)\text{Cl}$  (analogous to apatite); **dechenite**,  $[\text{Pb}, \text{Zn}](\text{VO}_3)_2$ ; **pucherite**,  $\text{BiVO}_4$ ; **volborthite**,  $[\text{Cu}, \text{Ca}]_3(\text{VO}_4)_2\text{H}_2\text{O}$ ; and **roscoelite**, a vanadium mica containing  $\text{V}_2\text{O}_3$ . **Carnotite**,  $\text{K}(\text{UO}_2)\text{VO}_4 \cdot 3/2\text{H}_2\text{O}$ , is also important as a source of uranium.



Columbium (also called niobium) and tantalum usually occur together, the principal minerals are columbite,  $\text{FeCb}_2\text{O}_6$ , and tantalite,  $\text{FeTa}_2\text{O}_6$ . Other minerals are: pyrochlor, calcium columbate, containing titanium, thorium and rare earths; yttrotantalite and fergusonite, complex oxide mixtures containing largely  $\text{Ta}_2\text{O}_5$ ,  $\text{Cb}_2\text{O}_5$ ,  $\text{Yt}_2\text{O}_3$ , and  $\text{Er}_2\text{O}_3$ .

**3. Metallurgy.**—**Vanadium** is extracted from its ores by leaching out the ore with strong hydrochloric acid, and is precipitated from this solution as ammonium vanadate by evaporation of the solution with excess of ammonium chloride. Ammonium vanadate, when roasted, yields the oxide.

The preparation of the pure metal is a difficult operation. The reduction of the pentoxide with carbon in an electric furnace yields mostly carbide; and the reduction with aluminum gives a mixture of the metal and dioxide. The reduction of the dichloride with hydrogen is a satisfactory method of preparing the metal on a small scale. Very little of the pure metal is prepared commercially, however, as the steel industry, which is the principal consumer, employs ferrovanadium. This is manufactured by the reduction of the mixed oxides with carbon in an electric furnace. A small amount of vanadium is consumed in making metavanadate for use as a catalyst in the manufacture of sulfuric acid.

The separation of pure **columbium** and **tantalum** oxides from their ores is largely an analytical problem (Par. 17). The metals may be prepared by the reduction of the complex alkali fluorides with sodium, or the oxide with metallic calcium or aluminum. At the temperature of the electric furnace, the oxides may be decomposed to the metals by heating in a vacuum. Reduction of the oxides with hydrogen is also employed. Tantalum may be electroplated from the fused complex potassium fluoride.

**4. The Metals.**—The more important physical properties are given in Table I. The metals are grey or silver white

TABLE I  
ATOMIC AND PHYSICAL PROPERTIES

	V	Cb	Ta
Atomic weight.....	50.95	92.91	180.88
Atomic numbers.....	23	41	73
Isotopes.....	51	93	181
Melting point, ° C. ....	1710	1950	2850
Boiling point, ° C. ....	3000 (?)	3300	4100 (?)
Density.....	5.9	8.4	16.6
Electrical resistivity, ohms-cm. at 25° C. ..			$15 \times 10^{-6}$
Ionization potential of gaseous atom, volts. .	6.71		
Tensile strength, lb. sq. in.....			130,000
Radius of metal ions $M^{+5}$ in crystals, cm. $\times 10^8$ .....	0.59	0.70	

in color, and do not tarnish readily. Though very hard, they may be rolled or hammered, and drawn into wire. Vanadium is used extensively in the steel industry (cf. **XIX—7**), to add tensile strength to steel. Columbium in the form of ferrocolumbium is employed in the manufacture of chromium steels to render them more weldable. Tantalum was formerly employed in electric light filaments, but has been replaced by tungsten. The metal, in spite of its electropositive character, is extremely resistant to chemical action at ordinary temperatures and is being employed as pipes, kettles, and containers in many chemical manufacturing processes, displacing platinum, and other expensive metals. Due to the passive nature of tantalum, it exhibits, to a high degree, an electrolytic valve action (see Aluminum, **VI—17**) and is employed in cells to act as current rectifiers. Tantalum absorbs gases readily at high temperatures; and becomes hard and brittle. For this reason, the metal must be worked cold or in a vacuum. Because of its hardness tantalum carbide is employed as a constituent of hard cutting-tool mixtures.

**5. Reactions of the Metals.**—The metals are attacked by oxygen only when heated. Vanadium is dissolved by nitric acid and other powerful oxidizing agents (Par. **6**);

but columbium and tantalum are attacked readily only by a mixture of nitric and hydrofluoric acids. The general reactions of the group are summarized in Table II.

TABLE II

## REACTIONS OF VANADIUM, COLUMBIUM, AND TANTALUM

$4M + 5O_2 = 2M_2O_5$	Heated. V also forms $VO_2$
$2M + 5X_2 = 2MX_5$	Heated. Ta and Cb with F, Cl, and Br. V forms only $VCl_4$ and $VBr_3$ .
$6M + 5N_2 = 2M_3N_5$	Heated. V forms VN
$M + C = MC$	High temperature
$M + 2S = MS_2$	Heated. V forms $V_2S_5$ also
$M + 5NaOH = NaMO_3 + \frac{5}{2}H_2$	
$+ 2Na_2O$	Fused. Ta and Cb form $Na_8M_6O_{19}$
$3M + 15HF + 5HNO_3 = 3H_2MOF_5$	
$+ 5NO + 7H_2O$	Also other complex fluo-acids
$2V + Si = V_2Si$	High temperature
$2Cb + H_2 = 2CbH$	

## VANADIUM COMPOUNDS

**6. Oxidation States.**—Vanadium forms compounds possessing the oxidation states 2, 3, 4, and 5. The two lower valences are basic; but the two higher are amphoteric, though in the aqueous solutions, the positive ions exist only as vanadyl,  $VO^{++}$ , and pervanadyl,  $V(OH)_4^+$ .

Oxidation-reduction potentials involving the various states are summarized below:

	VOLTS
$V = V^{++} + 2e^-$ .....	+ 1.5
$V^{++} = V^{+++} + e^-$ .....	+ 0.2
$V^{+++} + H_2O = VO^{++} + 2H^+ + e^-$ .....	- 0.314
$VO^{++} + 3H_2O = V(OH)_4^+ + 2H^+ + e^-$ .....	- 1.00

From these values, it follows that vanadic acid in concentrated hydrogen ion, i.e.  $V(OH)_4^+$  is a moderately powerful oxidizing agent; but the hydrogen ion is involved to such a high power that the potential decreases markedly in dilute acid, so that vanadate in neutral solution is not easily reduced. As the potentials indicated, the reduction products depend upon the strength of the reducing agent,

e.g.  $\text{Fe}^{++}$  gives  $\text{VO}^{++}$ ,  $\text{Sn}^{++}$  gives  $\text{V}^{+++}$ , and  $\text{Zn}$  gives  $\text{V}^{++}$ . Vanadous ion,  $\text{V}^{++}$ , is a strong reducing agent, and vanadic ion is fairly strong. The metal is oxidized by moderate oxidizing agents in acid solution to the +4 state and by powerful agents to vanadate.

**7. The +2 State.**—The monoxide,  $\text{VO}$ , is prepared by the reduction of vanadyl chloride,  $\text{VOCl}_2$ , by carbon, zinc, or hydrogen at red heat. The oxide is semi-metallic in appearance and was considered by Berzelius to be the metal. The **hydroxide**,  $\text{V}(\text{OH})_2$ , is but slightly soluble. Its salts in solution have a deep violet color. The **sulfate**,  $\text{VSO}_4$ , is prepared in solution by the reduction of sulfuric acid solutions of vanadates by zinc, or by cathodic reduction in an atmosphere of carbon dioxide. The solid hydrate,  $\text{VSO}_4 \cdot 7\text{H}_2\text{O}$ , may be obtained upon evaporation, and **double sulfates** are formed with the alkali sulfates,  $\text{M}_2\text{V}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The sulfate solution absorbs nitric oxide, similar to ferrous ion, and the **complex cyanide**,  $\text{V}(\text{CN})_6^{-4}$ , is similar to ferrocyanide in the solubilities of its salts. The anhydrous **chloride** and the **sulfide** are prepared, respectively, by the reactions:  $\text{VCl}_4 + \text{H}_2 = \text{VCl}_2 + 2\text{HCl}$ , and  $\text{V}_2\text{S}_3 + \text{H}_2 = 2\text{VS} + \text{H}_2\text{S}$ . The latter is not soluble in dilute hydrogen ion or in sulfide ion.

**8. The +3 State.**—In formulas and solubilities, the vanadic compounds resemble ferric, but unlike the latter, they are readily oxidized. The salts in solution are green; and the green **hydroxide**,  $\text{V}(\text{OH})_3$ , is precipitated from solutions of its salts by ammonia or alkali hydroxides. It is rapidly oxidized by air to form the dioxide. The **sesquioxide**,  $\text{V}_2\text{O}_3$ , may be obtained by reducing the pentoxide with hydrogen or carbon, and the product is insoluble in most acids. Solutions of the **halides** may be prepared by dissolving the hydroxide in the halogen acid. The anhydrous compounds may be prepared by reactions analogous to the following:  $2\text{VCl}_4 = 2\text{VCl}_3 + \text{Cl}_2$ , and  $\text{V}_2\text{O}_3 + 3\text{Br}_2 + \text{C} = 2\text{VBr}_3 + 3\text{CO}$ . The **oxychloride**,  $\text{VOCl}$ , is

but slightly soluble. Reduction of sulfuric acid solutions of the pentoxide gives **vanadic sulfate**,  $V_2(SO_4)_3$ , in solution; this salt readily forms alums. The oxide reacts when heated with ammonia, and with hydrogen sulfide, to give the **nitride**, VN, and the **sulfide**,  $V_2S_3$ , respectively. The latter is soluble in dilute acids.

Vanadic ion forms many complex and double salts, the most important being **double fluorides**, as  $(NH_4)_3VF_6$ , or  $(NH_4)_2VF_5$ ; **double oxalates** as,  $K_3V(C_2O_4)_3 \cdot 3H_2O$ ; complex cyanides as  $K_3V(CN)_6$ ; and sulfocyanides,  $K_3V(CNS)_6$ .

**9. The + 4 State.**—The **dioxide**,  $VO_2$ , may be obtained by partial reduction of the pentoxide; the **hydrous oxide**, is precipitated by the addition of sodium carbonate to vanadyl salts in solution. The hydrous oxide is oxidized in air. It is soluble in the alkali hydroxide and in ammonia, forming **vanadites**, e.g.  $K_2V_4O_9 \cdot 7H_2O$ . These compounds in solution have a deep black color, are not readily oxidized, and form slightly soluble vanadites with the heavy metals.

The dioxide dissolves in acid to form the blue vanadyl ion,  $VO^{++}$ , and many salts of this ion are known, e.g.,  $VOCl_2$ ,  $VOSO_4$ . The **anhydrous chloride** is formed by the reactions:  $V + 2Cl_2 = VCl_4$ , and  $VOCl_3 + 1/2Cl_2 + C = VCl_4 + CO$ . It is a heavy liquid with an extremely low melting point. The water solutions hydrolyze to vanadyl chloride. The addition of sulfide to an acid vanadyl solution precipitates the **sulfide**,  $VS_2$ , which is soluble in excess sulfide to form **thiovanadites**.

**10. The + 5 State.**—The **oxide**,  $V_2O_5$ , may be prepared by roasting ammonium metavanadate,  $NH_4VO_3$ ; or by the hydrolysis of pervanadyl chloride,  $VOCl_3$ . It is somewhat soluble in water to give a slightly acid solution, but with excess of hydrogen ion the acid forms pervanadyl ion,  $V(OH)_4^+$  (or  $VO_2^+$ ). **Metavanadic acid**,  $HVO_3$ , may be precipitated as golden yellow solid by the action of sulfurous acid upon copper vanadate. The acid is sometimes employed as gold bronze. **Pyrovanadic acid**,  $H_4V_2O_7$ ,



is precipitated by the addition of nitric acid to vanadate solutions.

The addition of alkali to vanadic acid results in the formation of complicated poly-anions.

Sodium salts of the **meta-**, **ortho-**, **pyro-**, and **hexa-vanadic** acids are known:  $\text{NaVO}_3$ ,  $\text{Na}_3\text{VO}_4$ ,  $\text{Na}_4\text{V}_2\text{O}_7$ ,  $\text{Na}_2\text{H}_2\text{V}_6\text{O}_{17}$ . The metavanadates of sodium, potassium, ammonium, barium, and lead are but slightly soluble in cold water; but salts of other positive ions are soluble, and the color is generally yellow. The alkali pyrovanadates are soluble. In solution orthovanadate is readily hydrolyzed:  $2\text{VO}_4^{--} + \text{H}_2\text{O} = \text{V}_2\text{O}_7^{----} + 2\text{OH}^-$ . At high temperatures, the ortho salts are stable, however, and constitute many of the vanadium minerals. The most important compound is probably ammonium metavanadate,  $\text{NH}_4\text{VO}_3$ , which is precipitated by excess ammonium chloride from meta- and pyrovanadate solutions. In recent years large quantities of the salt have been used in the preparation of the vanadium catalysts for the manufacture of sulfuric acid.

The alkali metavanadates are readily converted to **peroxyvanadates**,  $\text{MVO}_4$ , by hydrogen peroxide; and peroxyvanadic acid,  $\text{HVO}_4$ , is formed when the pentoxide is added to a solution of hydrogen peroxide in sulfuric acid. The solution has a deep red color.

Of the pervanadyl compounds, the most important is probably the **pervanadyl sulfate**,  $(\text{VO})_2(\text{SO}_4)_3$ . This may be obtained as a red-brown solid upon evaporating the acid solution, and basic salts as,  $\text{VO}(\text{OH})\text{SO}_4$ , are also formed. With concentrated hydrochloric acid, chlorine is evolved and the dioxide formed. However, the **pervanadyl chloride** may be made by the action of chlorine upon  $\text{VO}$  or  $\text{V}_2\text{O}_3$ , or upon a heated mixture of the pentoxide and carbon. The chloride is a heavy low melting liquid with a lemon-yellow color. It fumes in moist air and is hydrolyzed by water to vanadic acid. **Complex oxyfluovanadates**, as  $\text{K}_2\text{VOF}_5$  and  $\text{K}_2\text{VO}_2\text{F}_3$ , are precipitated by the addition



of potassium fluoride to the pervanadyl fluoride solutions.

Ammonium sulfide acts upon vanadate solutions to form **thiovanadate**,  $\text{VS}_4^{---}$ . The addition of acid to this solution precipitates the **sulfide**,  $\text{V}_2\text{S}_5$ , or possibly a mixture of  $\text{V}_2\text{S}_5$  and  $\text{VS}_2$ .

## COLUMBIUM COMPOUNDS

**11. Oxidation States.**—The compounds of lower states are much less stable than in the case of vanadium. The only + 5 compounds which may be obtained in acid solution are the complex fluoride and chloride, and these solutions may be reduced quantitatively by zinc in the cold to a blue solution of the + 3 columbium; but, if the solution is heated, a precipitate of mixed oxides, possibly  $\text{CbO}_2$  and  $\text{Cb}_2\text{O}_3$ , is formed. The + 3 compounds in solution are oxidized very rapidly by oxygen. The oxychloride,  $\text{CbOCl}_3$ , may be reduced by sodium to the monoxide,  $\text{CbO}$ , which dissolves in acid with the liberation of hydrogen. The pentoxide may be reduced by magnesium to the dioxide,  $\text{CbO}_2$ , which is not attacked by acids, but burns in air when heated.

Due to the passivity of the metal and the inertness of the oxide, very little is known about the true oxidation-reduction potentials of columbium, and the following values are calculated from thermal data.

	VOLTS
$2\text{Cb} + 5\text{H}_2\text{O} = \text{Cb}_2\text{O}_5 + 10\text{H}^+ + 10e^-$ .....	0.62
$\text{Cb} = \text{Cb}^{+++} + 3e^-$ .....	<i>ca.</i> 1.1

**12. Pentoxide and Columbates.**—The pentoxide,  $\text{Cb}_2\text{O}_5$ , may be prepared by decomposing the potassium oxyfluoride with sulfuric acid. With concentrated acid the oxide dissolves with the formation of some complex ion, possibly  $\text{Cb}(\text{SO}_4)_3^-$ . The pentachloride hydrolyzes in water to give the **meta-acid**,  $\text{HCbO}_3$ . The oxide and acid when fused

with alkalies or alkali carbonates yield complex columbates. **Potassium hexacolumbate**,  $\text{K}_8\text{Cb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ , is readily soluble in water, and with excess of alkali forms a number of other salts, such as  $\text{K}_4\text{Cb}_2\text{O}_7\cdot 11\text{H}_2\text{O}$ .

**Peroxycolumbates** are formed by the action of peroxides upon columbates; and the **peroxy-acid**,  $\text{HCbO}_4$ , is obtained as a yellow solid when columbic acid is warmed with hydrogen peroxide.

**Halogen Compounds.**—Columbic acid is soluble in hydrofluoric acid; the addition of potassium fluoride to the solution yields **fluocolumbate**,  $\text{K}_2\text{CbF}_7$ , and in less concentrated acid double salts of the oxyfluoride, such as  $\text{K}_2\text{CbOF}_5$ .

The **pentachloride**,  $\text{CbCl}_5$ , is formed by passing chlorine over a heated mixture of the oxide and carbon; or sulfur chloride,  $\text{S}_2\text{Cl}_2$ , over the oxide. The pentachloride is soluble in hydrochloric acid. The **oxychloride** is a volatile solid, and like the chloride, is completely hydrolyzed in water. Corresponding compounds of fluorine and bromine have also been prepared, which have rather similar properties.

At red heat, the pentachloride decomposes into the **trichloride**,  $\text{CbCl}_3$ . This anhydrous chloride is not decomposed by water, but is readily oxidized with nitric acid, and when heated reacts with carbon dioxide:  $\text{CbCl}_3 + \text{CO}_2 = \text{CbOCl}_3 + \text{CO}$ .

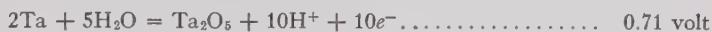
**Other Compounds.**—The metal heated in nitrogen at  $1200^\circ$  forms the **nitride**,  $\text{Cb}_3\text{N}_5$ . Mixed oxide-nitride compounds result from the action of ammonia upon the oxide at red heat.

The metal unites with hydrogen when heated to form the **hydride**,  $\text{CbH}$ , which is not attacked by acids, but readily burns in air.

The oxide is not converted into sulfide by ammonium sulfide, but oxysulfides, e.g.,  $\text{Cb}_2\text{O}_2\text{S}_3$ ,  $\text{CbOS}_3$ , form when the oxide is heated in an atmosphere of carbon dioxide and carbon disulfide.

## TANTALUM COMPOUNDS

**13.** Although there is very little experimental work on the oxidation-reduction potentials of tantalum, the value for the heat of formation of the pentoxide,  $-484,500$  cal., leads to the following approximate potential:



No compounds of lower oxidation states are stable in aqueous solution. The  $+2$  chloride has been prepared at high temperatures, but the water solution evolves hydrogen rapidly.

**14. Pentoxide and Tantalates.**—The pentoxide,  $\text{Ta}_2\text{O}_5$ , is formed when the metal burns in air. It is left as a residue when tantalates are fused with potassium acid sulfate, and the product extracted with hydrochloric acid. The oxide is very inert, but when fused with alkali hydroxides forms **hexatantalates**, e.g.  $\text{Na}_8\text{Ta}_6\text{O}_{19} \cdot 25\text{H}_2\text{O}$ . These compounds are soluble in water. When ignited with ammonium chloride, **metatantalates**, e.g.  $\text{NaTaO}_3$ , are formed; these are not soluble. The **meta-acid**,  $\text{HTaO}_3$ , is precipitated when the pentachloride is added to water.

A solution of potassium hexatantalate gives with peroxide a **peroxytantalate**,  $\text{K}_3\text{TaO}_8 \cdot 1/2\text{H}_2\text{O}$ , which may be precipitated from the solution by the addition of alcohol. The compound is decomposed by sulfuric acid to give the acid,  $\text{HTaO}_4$ , which is fairly stable.

The pentoxide reduced with magnesium yields a **mon-oxide**,  $\text{TaO}$ , which is not soluble in acids, and burns in air to the pentoxide.

The ignited pentoxide is not soluble in any acid, but the hydrated oxide dissolves in hydrofluoric acid, and either dissolves slightly, or is peptized by other acids.

**15. Compounds with the Halogens.**—The **pentafluoride**, **chloride**, and **bromide**, form when the metal is heated in the corresponding halogen. Alkali **fluotantalates**, e.g.

$K_2TaF_7$ , are obtained by dissolving the hydrated pentoxide in hydrofluoric acid, and adding alkali fluoride. These compounds are easily soluble in hot water, but much less soluble in cold. When the solution of the potassium salts is boiled, an **oxyfluoride**,  $K_4Ta_4O_5F_{14}$ , precipitates.

The pentachloride and bromide are most readily prepared by heating a mixture of the oxide and carbon in a stream of chlorine. These compounds are readily volatile around  $150^\circ$ , and are completely hydrolyzed by water.

**16. Other Compounds.**—The **sulfide**,  $TaS_2$ , is said to be formed by the action of hydrogen and carbon disulfide upon the heated oxide. It is not soluble in hydrogen ion. When the chloride is heated in ammonia at not too high a temperature, a bright red **nitride**,  $Ta_3N_5$ , is formed. At higher temperatures, the compound  $TaN$  is produced. The pentanitride is also formed when the metal is heated in nitrogen at  $1000^\circ C$ .

The **carbide**,  $TaC$ , forms when the oxide is reduced with carbon at high temperatures.

**17. Analytical.**—The slight solubility of the oxides of vanadium, columbium, and tantalum in dilute hydrogen ion, and in oxidizing agents, and their ready solubility in hydrofluoric acid, places them analytically in a group consisting of  $Sb_2O_5$ ,  $SnO_2$ ,  $WO_3$ ,  $MoO_3$ ,  $TeO_2$ ,  $V_2O_4$ ,  $TiO_2$ ,  $Ta_2O_5$ ,  $Cb_2O_5$ , and  $Bi_2O_3$ , together with phosphates of Sn, Ti, and Zr. When these oxides are dissolved in hydrofluoric acid and treated with ammonium sulfide, a separation is obtained, giving in the filtrate, the thio-salts of Sb, Sn, W, Mo, Te, V, and a residue of  $TiO_2$ ,  $Ta_2O_5$ ,  $Cb_2O_5$ ,  $Bi_2O_3$ , and Ti and Zr phosphate or vanadate. The presence of vanadium in the thio-salt solution is recognized by the violet-red color of  $(NH_4)_3VS_4$ .

When the  $TiO_2$ ,  $Ta_2O_5$ , etc. residue above is boiled with sodium salicylate solution, the titanium and vanadium are extracted. The residue is fused with  $K_2CO_3$ ; and  $K_8Ta_3O_{18}$  and  $K_8Cb_3O_{18}$  are obtained in solution by extracting with

cold water. The tantalum is separated from the columbium by the smaller solubility of the potassium oxyfluotantalate, and the columbium recognized by reduction to  $\text{CbCl}_3$ , blue, with zinc, and the reaction of this solution with mercuric chloride to give mercurous chloride.

In gravimetric determinations, these elements are usually separated and weighed as the pentoxides. Vanadium and columbium are determined volumetrically by reduction to vanadyl and to the  $+3$  columbium, and titration with permanganate.

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# Chapter XVII

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## SUBGROUP VI. CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM

1. The elements of Subgroup VI have 6 as the maximum positive oxidation state and in this state show many properties common to each other, as well as to sulfur in the sulfates. In addition, the elements of the group have a variety of lower oxidation states, in which they do not resemble each other as much as they do the elements of higher and lower atomic numbers; especially is this true of chromium, whose lower states are similar to the corresponding ones of vanadium and manganese. This fact is to be correlated with the position of the elements in transition series in which an eight electron shell is being converted to an eighteen electron shell (Append. XVIII). One of the most striking properties of the  $+6$  compounds is the tendency to form poly-acids. This tendency reaches a maximum in molybdenum, which forms acids containing many molecules of the trioxide. The acidic nature of the oxides decreases with increasing size of the ions.

The metals have very high melting points, that of tungsten being higher than that of any other metal. They are also very tough, and advantage is taken of this in forming many important alloys with iron. Uranium is highly electropositive, the others somewhat so.

Uranium is radioactive; this property is discussed in connection with the other radioactive elements, Chapter **XXI**.



**2. Occurrence.**—The metals do not occur free in nature. Chromium is the most abundant of the group, and is present to the average extent of about 0.037 per cent in igneous rocks, usually as  $\text{Cr}_2\text{O}_3$ , replacing  $\text{Al}_2\text{O}_3$  in aluminates. The estimated percentages of the others are: molybdenum  $10^{-6}$ , tungsten  $5 \times 10^{-5}$ , and uranium  $8 \times 10^{-5}$ . The value for uranium is remarkably high in comparison to the other heavy elements. The most important chromium ore is **chromite**,  $\text{Fe}(\text{Cr}_2\text{O}_4)$ , or  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ . Lead chromate,  $\text{PbCrO}_4$ , and other chromates of the heavy metals also occur.

Molybdenum is most frequently found as the sulfide, **molybdenite**,  $\text{MoS}_2$ , which resembles graphite in appearance. It also occurs as molybdates, especially  $\text{PbMoO}_4$  and  $\text{Fe}_2(\text{MoO}_4)_3 \cdot 7.5\text{H}_2\text{O}$ .

The most important tungsten ore is **wolframite**, an isomorphous ferrous-manganous tungstate,  $[\text{Fe}, \text{Mn}]\text{WO}_4$ . Other tungstates, as  $\text{CaWO}_4$ ,  $\text{PbWO}_4$ , and  $\text{CuWO}_4$ , and the trioxide,  $\text{WO}_3$ , or wolfram ochre, are also found.

Uranium is found as **pitchblende** or **uraninite**, which is about 80 per cent  $\text{U}_3\text{O}_8$ , together with the rare earth and other oxides; and as **carnotite**,  $\text{K}(\text{UO}_2)\text{VO}_4 \cdot 3/2\text{H}_2\text{O}$  and **autunite**,  $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ .

## METALS AND METALLURGY

**3. Chromium.**—The greater portion of metallic chromium is utilized in chrome steel, and for this use ferrochrome is prepared by the direct reduction of chromite by carbon:  $\text{FeCr}_2\text{O}_4 + 4\text{C} = \text{Fe} + 2\text{Cr} + 4\text{CO}$ . For the preparation of chromium compounds, the ore is usually fused with sodium carbonate in air:  $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 8\text{Na}_2\text{CrO}_4 + 8\text{CO}_2$ ; the sodium chromate is then extracted with water. The pure metal is conveniently prepared by reducing chromic oxide with aluminum (Goldschmidt reaction), or with carbon in an electric furnace. The electrolytic deposition of chromium on iron or copper

has recently assumed importance. The electrolyte used is an acid chromic chromate solution containing sulfate, phosphate, borate, or other acid radicals.

Chromium is similar to platinum in luster, and this together with its high resistance to corrosion, has resulted in the use of the electroplated metal on motor cars and miscellaneous domestic appliances.

**Chrome steel** (0.5 to 1.0 per cent Cr, 0.75 per cent Si, and 0.5–1.25 per cent Mn) is very hard and tough. **Stainless steel** (14 per cent Cr) is used in the manufacture of cutlery, valves, turbine blades, etc. **Nichrome** (60 per cent Ni, 15 per cent Cr, and 25 per cent Fe) is used as resistance wire in electrical heaters. Chromium, with cobalt and tungsten, or molybdenum, forms an alloy known as **stellite**, suitable for high-speed tools (cf. XIX—19).

It is estimated that 50 per cent of the American consumption of chromate is for metallurgical industries, 40 per cent for the manufacture of refractory chrome-brick for furnace lining, and 10 per cent for the chemical industries.

**4. Molybdenum.**—The sulfide ore is generally roasted to the trioxide which is then extracted with ammonia. Solid ammonium molybdate is obtained when the solution is evaporated, and this yields the trioxide upon ignition. The metal is prepared by the reduction of the oxide by carbon in an electric furnace, or by the reduction of the oxide or chloride by hydrogen. Molybdenum is silver white in color, tough, and ductile. It is added to steel as a toughener; the addition of 1 per cent of molybdenum doubles the strength of low carbon steels at temperatures above 475° C.

**5. Tungsten.**—Tungsten is generally obtained from wolframite ores by fusion with sodium carbonate, to convert to sodium tungstate, which is then extracted with water, and the solution digested with hydrochloric acid to precipitate tungstic acid. The acid is reduced by heating strongly with carbon, but the product is a powder, as the temperature is far below the melting point of the metal. Rods of the metal

are formed by sintering the particles together by passing a strong electric current through the compressed powder. Tungsten has become one of the most important industrial metals. In 1936 three quarters of a billion tungsten filament electric lamps were sold in the United States. In

TABLE I  
ATOMIC AND PHYSICAL PROPERTIES

	Cr	Mo	W	U
Atomic weight.....	52.01	95.95	183.92	238.07
Atomic number.....	24	42	74	92
Isotopes.....	50, 52, 53, 54	92, 94, 95, 96, 97, 98, 100	182, 183, 184, 186	234, 235, 238
Density.....	7.1	10.2	19.3	18.7
Melting point, ° C.....	1550	2620	3370	1850
Boiling point, ° C.....	2475	4800	5930	
Tensile strength, lbs. per sq. in.....			590,000	
Electrical resistivity, ohm-cm.....	$2.6 \times 10^{-6}$	$4.8 \times 10^{-6}$	$5.5 \times 10^{-6}$	$6.0 \times 10^{-6}$
Ionization potential, volts.....	6.74	7.35		
Radius of $M^{+6}$ ion in crys- tals, cm. $\times 10^8$ .....	0.52	0.62		

order to draw the metal into wire, it is necessary to subject the rod to severe working at a low temperature to break up the large crystals which form when the metal is heated and render it brittle. The tensile strength of the drawn wire exceeds that of any other metallic substance. The metal is also used as contact joints for making and breaking electrical circuits, for internal combustion engine valves, X-ray apparatus and utensils. The metal may be electroplated from solutions of sodium tungstate, but the best coatings are secured by deposition with nickel (or other metals). The nickel-tungsten (35-50 per cent W) alloy surfaces have remarkable resistance to chemical action.

Ferro-tungsten can be prepared by the reduction of the purer forms of iron tungstate ore with carbon. It is em-

ployed in the manufacture of tool-steel (see Chromium) and other tungsten steels (see Iron).

**6. Uranium.**—In the extraction of uranium from pitchblende, the ore is generally roasted with alkali carbonate and some nitrate to convert the oxide,  $U_3O_8$ , into alkali uranate. After washing with water the ore is treated with sulfuric acid, which dissolves out the uranium as uranyl sulfate,  $UO_2SO_4$ . The metal is prepared by the reduction of the oxides by carbon in an electric furnace or by the electrolysis of the fused potassium uranium fluoride. Uranium is a heavy "white" metal with a much lower melting point than tungsten. It is highly electropositive and has no important commercial applications but finds some use in alloys.

TABLE II  
REACTION PRODUCTS OF THE ELEMENTS

REACTION WITH	Cr	Mo	W	U
$O_2$	$Cr_2O_3$	$MoO_3$	$WO_3$	$UO_3, U_3O_8$
$F_2$	$CrF_3$	$MoF_6$	$WF_6$	$UF_4, UF_6$
$Cl_2$	$CrCl_3$	$MoCl_5$	$WCl_6$	$UCl_4, UCl_5$
$Br_2$	$CrBr_3$	$MoBr_4$	$WBr_6$	$UBr_5$
$I_2$	$CrI_2$	No action at $500^\circ$	$WI_2$	$UI_4$
$H^+$	$Cr^{++}, Cr^{+++}$ (slow)	No action	No action	$U^{+4}$
$OH^-$	$CrO_2^-$ (slow)	No action	$WO_4^{--}$	$UO_2$
$HNO_3$	$Cr^{+++}$	$MoO_3$	$WO_3$	$UO_2^{++}$
C	$Cr_2C_3$	$Mo_2C, MoC$	$W_2C, WC$	$U_2C_3$
$N_2$	$CrN$	No action at $1000^\circ$	No action at $2000^\circ$ , $WN_2$ at $2500^\circ$	$U_2N_4$
S	$CrS$	$MoS_2, Mo_2S_3$	$WS_2$	$US_2$
B	$CrB, Cr_3B$	$Mo_3B_4$	$WB_2$	$UB_2$

**7. Reactions of the Metals.**—The reactions of the metals with common reagents are so varied in nature as to render them difficult to summarize in the form of general group reactions; however, the principal reaction products have

been summarized in Table II. The lighter members of the group exhibit to a high degree the property of passivity, and their reactions with powerful oxidizing agents are thus often extremely slow.

## COMPOUNDS OF CHROMIUM

**8. Oxidation States.**—Chromium forms compounds in which it has the oxidation numbers + 2 (chromous), + 3 (chromic), and + 6 (chromate). The + 2 state is basic, the + 3 state is amphoteric, and the + 6 state is acidic. The potential relations between the states are summarized in the following half reactions:

	VOLTS
$\text{Cr} = \text{Cr}^{++} + 2e^-$ .....	+ 0.86
$\text{Cr}^{++} = \text{Cr}^{+++} + e^-$ .....	+ 0.41
$2\text{Cr}^{+++} + 7\text{H}_2\text{O} = \text{Cr}_2\text{O}_7^{--} + 14\text{H}^+ + 6e^-$ .....	- 1.36

It is evident from these values that the chromate in acid solution is a powerful oxidizing agent. The equilibrium,  $\text{Cr} + 2\text{Cr}^{+++} = 3\text{Cr}^{++}$ , favors the formation of chromous ion, but the latter is such a powerful reducing agent that its solutions are oxidized even by very weak oxidizing agents to chromic ion.

**9. Chromous Compounds.**—Chromous compounds are somewhat similar to ferrous. **Chromous hydroxide**,  $\text{Cr}(\text{OH})_2$ , is a slightly soluble, brownish yellow substance, which is oxidized readily in air and when heated liberates hydrogen:  $2\text{Cr}(\text{OH})_2 = \text{Cr}_2\text{O}_3 + \text{H}_2\text{O} + \text{H}_2$ . Solutions of chromous ion are blue, and may be prepared by the reduction of chromic solutions by the metal or by zinc (see above). The **chloride** and **sulfate** are soluble. The former may be prepared as an anhydrous salt, by heating the metal in hydrogen chloride. The **sulfide**,  $\text{CrS}$ , and **carbonate**,  $\text{CrCO}_3$ , are but slightly soluble, and the **acetate**,  $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_2$ , but moderately so.

**10. Chromic Compounds.**—The **oxide**,  $\text{Cr}_2\text{O}_3$ , is the most stable of the chromium oxides, and is formed by heating the

metal or other oxides in air. Due to its fine green color it is used as a pigment, **chrome oxide green**. This is generally prepared by igniting sodium dichromate with sulfur or ammonium chloride:  $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{S} = \text{Cr}_2\text{O}_3 + \text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{NH}_4\text{Cl} = \text{Cr}_2\text{O}_3 + 2\text{NaCl} + \text{N}_2 + 4\text{H}_2\text{O}$ . The oxide is isomorphous with corundum,  $\text{Al}_2\text{O}_3$ . A **hydrated oxide**,  $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , may be formed by hydrolysis under pressure, but there is no evidence for the existence of  $\text{Cr}(\text{OH})_3$ . The so-called "hydroxide" which is precipitated from chromic solution, may best be described as a **hydrous oxide**.

In its amphoteric properties the hydrous oxide,  $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ , resembles aluminum hydroxide, and like the latter is precipitated by ammonium hydroxide, and by solutions of alkali sulfides and carbonates. Excess of alkali hydroxide dissolves the precipitate with the formation of **chromites**, but the hydroxide or hydrated oxide is precipitated upon boiling. Chromites are readily formed by fusing the oxide with metal oxides, and such compounds constitute the common chromium minerals, the most important being **ferrous chromite**,  $\text{FeCr}_2\text{O}_4$ . Chromite is used extensively as a refractory, especially in lining open-hearth furnaces used in the manufacture of steel.

11. Chromic ion forms numerous coordination complexes, especially with ammonia, water, halides, cyanide, and thiocyanate. A number of these are tabulated below. The coordination number of chromium is six. In solution these compounds dissociate into the complex ion and the ions placed outside the bracket.

$[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$	$[\text{Cr}(\text{NH}_3)_6](\text{CNS})_3$	$[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$
$[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	$[\text{Cr}(\text{NH}_3)_3(\text{CNS})_3]$	$[\text{Cr}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$
$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	$[\text{Cr}(\text{CNS})_6]\text{K}_3$	$[\text{Cr}_4\text{O}(\text{SO}_4)_4]\text{SO}_4$
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$	$[\text{Cr}(\text{CN})_6]\text{K}_3$	$[\text{Cr}(\text{OH})(\text{NH}_3)_5]\text{Br}_2$

The two water-chloride complexes are of especial interest. The complex ion,  $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$ , has a violet color, and is



present largely in dilute chromic ion solutions, while the complex,  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ , is green and forms in more concentrated solutions in presence of excess chloride. The rates of transition are slow, however, and the two ions may be obtained in the same solution. Only one third of the chloride may be precipitated from the green solution by silver ion.

**12. Chromic sulfate**,  $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , may be precipitated by the addition of alcohol to a solution made by dissolving the oxide in sulfuric acid. This solution is violet, probably  $\text{Cr}(\text{H}_2\text{O})_6^{+++}$ , *vide supra*, but upon heating a green sulfate solution is formed, which does not form a precipitate upon the addition of alcohol, and in which only one third of the sulfate is ionized. Upon standing, the green solution reverts to the blue. Chromic sulfate readily forms **alums**, e.g.,  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

**Chromic phosphate**,  $\text{CrPO}_4 \cdot 6\text{H}_2\text{O}$ , precipitates when sodium hydrogen phosphate is added to a chromic solution. Several other hydrates are formed by carrying out the precipitation at higher temperatures.

**13. Chromic Acid and Derivatives.**—**Chromic anhydride**, or chromium trioxide, separates as a mass of scarlet needles when a cold concentrated solution of potassium dichromate is treated with concentrated sulfuric acid. It melts without decomposition, but loses oxygen around  $250^\circ$  to form the oxide,  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ , or  $\text{CrO}_2$ , and at higher temperatures,  $\text{Cr}_2\text{O}_3$ . The trioxide is very soluble in water, forming **chromic** and **dichromic acids**,  $\text{H}_2\text{CrO}_4$  and  $\text{H}_2\text{Cr}_2\text{O}_7$ . The former may be crystallized from warm concentrated solutions. A solution of chromic acid, formed by adding sulfuric acid to sodium dichromate, is frequently used in the laboratory as “**cleaning solution**.”

Like the other members of the sixth periodic group, chromate forms complexes containing varying amounts of the trioxide; and the potassium salts,  $\text{K}_2\text{CrO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{K}_2\text{Cr}_3\text{O}_{10}$ , and  $\text{K}_2\text{Cr}_4\text{O}_{13}$  are known. However, only the

first two are important, the chromate existing in alkaline solution, and the dichromate in acid solutions. The equilibrium between the two ions is represented by the equation:  $2\text{CrO}_4^{--} + 2\text{H}^+ = \text{Cr}_2\text{O}_7^{--} + \text{H}_2\text{O}$ ,  $K = 4.2 \times 10^{14}$ . The mechanism of the equilibrium involves the two equilibria:  $\text{HCrO}_4^- = \text{CrO}_4^{--} + \text{H}^+$ ,  $K = 3.2 \times 10^{-7}$ , and  $2\text{HCrO}_4^- = \text{H}_2\text{O} + \text{Cr}_2\text{O}_7^{--}$ ,  $K = 43$ .

The **alkali chromates** are prepared from chromite by roasting the ore with the alkali carbonate, or mixtures of limestone and alkali sulfate:  $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 8\text{Na}_2\text{CrO}_4 + 8\text{CO}_2$ . The cinder is then crushed and extracted with water to obtain the chromate. **Sodium chromate** crystallizes as  $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$ , isomorphous with the sulfate, and changes to the hexahydrate at  $79.5^\circ$ . **Potassium chromate**,  $\text{K}_2\text{CrO}_4$ , is isomorphous with potassium sulfate.

**Sodium dichromate**,  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , is obtained from the chromate by adding acid and crystallizing from the acid solution. Above  $82^\circ$ , the anhydrous salt separates. **Potassium dichromate** is prepared in a similar way. It is not very soluble in cold water, but readily soluble in hot. **Ammonium dichromate**,  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ , is generally made from chromic acid and ammonia. Upon heating, it decomposes according to the equation:  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 = \text{Cr}_2\text{O}_3 + \text{N}_2 + 4\text{H}_2\text{O}$ .

Dichromates are employed extensively in processes requiring a strong oxidizing agent. In the chrome-tanning process, the hide is treated with sodium dichromate, which is then reduced, and chromic hydroxide precipitated in the pores of the leather. Dichromate forms with gelatine, when exposed to the light, an insoluble product, and advantage is taken of this fact in a number of photographic processes. Potassium dichromate is important in analytical chemistry in the titration of reducing agents, especially ferrous salts (cf. XIX—16).

A number of slightly soluble chromates are important pigments: e.g. **chrome yellow**,  $\text{PbCrO}_4$ ; **chrome orange**,  $\text{Pb}_2\text{Cr}_2\text{O}_7$ .

$\text{OCrO}_4$ ; **zinc yellow** approximately  $\text{K}_2\text{O} \cdot 4\text{ZnCrO}_4 \cdot 3\text{H}_2\text{O}$ . In general, the solubilities of the chromates are very similar to those of the sulfates.

**14. Chromyl Compounds.**—**Chromyl chloride**,  $\text{CrO}_2\text{Cl}_2$ , and **fluoride**,  $\text{CrO}_2\text{F}_2$ , may be prepared by distilling dichromate with the alkali halide and sulfuric acid. The chloride is a blood-red liquid, which is hydrolyzed by water to chromic and hydrochloric acids. Intermediate **chlor-chromates** also exist, e.g.  $\text{KCrO}_3\text{Cl}$ , and the halides may be replaced from the chromyl compounds with ammonia to form **chromyl diamide**,  $\text{CrO}_2(\text{NH}_2)_2$ .

**15. Peroxychromates.**—Hydrogen peroxide gives with chromate in acid a deep blue solution of peroxychromate. If this solution is shaken with ether, the peroxy-acid is extracted. This constitutes a very delicate test for chromate or for hydrogen peroxide. The exact composition of the acid is uncertain but appears to be  $\text{CrO}_5$ . With alkalis it gives salts which are thought to have formulas such as  $\text{K}_2\text{Cr}_2\text{O}_{12}$ . At low temperatures in alkaline solution red peroxy-salts such as  $\text{K}_6\text{Cr}_2\text{O}_{16}$  are formed. From ammoniacal solutions the compound  $\text{CrO}_4 \cdot 3\text{NH}_3$  has been prepared.

## COMPOUNDS OF MOLYBDENUM

**16. Oxidation States.**—Molybdenum forms compounds having the positive oxidation states 2, 3, 4, 5, and 6; however, the + 2 and + 4 compounds exist in water solutions only in the form of a few relatively unstable complex ions. Approximate values of the oxidation-reduction potentials for the other states in acid solution are given below.

	VOLTS
$\text{Mo} + 3\text{H}_2\text{O} = \text{MoO}_3 + 6\text{H}^+ + 6e^-$ .....	- 0.1
$\text{MoO}_2^+ + 2\text{H}_2\text{O} = \text{H}_2\text{MoO}_4(\text{aq}) + 2\text{H}^+ + 2e^-$ .....	<i>ca.</i> - 0.4
$\text{Mo}^{+++} + \text{H}_2\text{O} = \text{MoO}_2^+ + 4\text{H}^+ + 2e^-$ .....	<i>ca.</i> 0.0
$\text{Mo} = \text{Mo}^{+++} + 3e^-$ .....	<i>ca.</i> 0.2

**17. The + 2 State.**—The **dichloride**,  $\text{MoCl}_2$ , is formed by heating the trichloride:  $2\text{MoCl}_3 = \text{MoCl}_2 + \text{MoCl}_4$ .

The **bromide** may be prepared in a similar manner, and the iodide by heating the pentachloride in hydrogen iodide. These halides are insoluble in water but dissolve in alkalis, and upon acidifying the solution, precipitate the complex bases  $(\text{Mo}_3\text{X}_4)(\text{OH})_2$ . The halides appear to be derivative of the same complex having the formula  $\text{Mo}_3\text{X}_6$ , or  $[\text{Mo}_3\text{X}_4]\text{-X}_2$ . They are slowly oxidized by water.

**18. The + 3 State.**—Solutions of + 3 molybdenum are prepared by the reduction of molybdic acid by powerful reducing agents. The color of the solutions is generally an olive green. The **hydroxide**,  $\text{Mo}(\text{OH})_3$ , (or hydrous oxide) is black, and insoluble in water or excess hydroxide. Upon ignition, it gives the **oxide**,  $\text{Mo}_2\text{O}_3$ . Ammonium sulfide precipitates the **sulfide**,  $\text{Mo}_2\text{S}_3$ , soluble in excess of the reagent. The **phosphate** is also but slightly soluble. Complex ions are formed with halides, and with thiocyanate, e.g.  $\text{K}_3\text{MoCl}_6$  and  $\text{K}_3\text{Mo}(\text{CNS})_6$ ; and the colors of these solutions vary from red to violet.

**19. The + 4 State.**—The **sulfide**,  $\text{MoS}_2$ , is the principal ore of the element. The **oxide**,  $\text{MoO}_2$ , forms when the sesquioxide is heated in air, or the trioxide is reduced with hydrogen ( $500^\circ$ ) or carbon ( $700^\circ$ ). The chloride, bromide, and iodide may be prepared mixed with the dihalide, by heating the trihalide. These compounds are not soluble in water, and the + 4 ion is not stable, probably being oxidized and reduced to  $\text{MoO}^{+++}$  and  $\text{Mo}^{+++}$ . However, a number of water soluble complex cyanide and halide compounds have been prepared, e.g.,  $\text{K}_4\text{Mo}(\text{CN})_8$ ,  $\text{K}_4\text{MoO}_2(\text{CN})_4$ , and  $\text{H}_n\text{MoI}_{4+n}$ .

**20. The + 5 State.**—The **pentachloride**,  $\text{MoCl}_5$ , is made by heating the metal or lower chloride in chlorine. It is the only known oxygen-free compound of this state. In water, it hydrolyzes to the molybdenyl compound:  $\text{MoCl}_5 + \text{H}_2\text{O} = \text{MoOCl}_3 + 2\text{HCl}$ . Compounds of the common acids, with  $\text{MoO}^{+++}$  or  $\text{MO}_2^+$ , are prepared by the reduction of molybdate in acid solution with moderately strong re-

ducing agents, e.g.  $\text{SnCl}_2$ . The addition of hydroxide to the solutions precipitates the **hydroxide**,  $\text{MoO}(\text{OH})_3$ , which may be decomposed to the **pentoxide**,  $\text{Mo}_2\text{O}_5$ . A delicate test for + 5 molybdenum is the formation of a deep red colored solution upon the addition of thiocyanate, probably  $\text{Mo}(\text{OH})_2(\text{CNS})_3$ . Mild reducing agents act upon an excess of molybdic acid with the production of a deep blue precipitate, **molybdenum blue**, which appears to be a molybdenyl molybdate,  $(\text{MoO})_3(\text{MoO}_4)_2$ , or  $(\text{MoO}_2)_2\text{MoO}_4$ . In high acid concentration the reduction forms an ion, probably  $\text{MoO}_2^+$ . A number of complex chlorides, e.g.  $\text{MoOCl}_5^{--}$  and  $\text{MoOCl}_4^-$  are known.

**21. The + 6 State.**—The **trioxide**,  $\text{MoO}_3$ , is a white solid which is soluble, one part in 500 parts of cold water, forming a slightly acid solution. The oxide is formed by roasting the disulfide in air, by the igniting of ammonium molybdate, or by the decomposition of a molybdate with hot nitric acid. In the latter case, if the solution is allowed to crystallize in the cold, yellow **molybdic acid**,  $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ , separates.

The oxide forms normal **molybdates**, e.g.  $\text{Na}_2\text{MoO}_4$ , especially if fused with basic oxides or carbonates; but these normal salts are in general unstable, if soluble in water, and tend to form **polymolybdates**. The complexity of the polyion depends upon the hydrogen ion concentration and the following values have been given: pH, 14–6.5,  $\text{MoO}_4^{-2}$ ; pH, 6.3–4.5,  $(\text{Mo}_3\text{O}_{11})^{-4}$ ; pH 4.5–1.5,  $(\text{Mo}_6\text{O}_{21})^{-6}$ ; pH, 1.25,  $(\text{Mo}_{12}\text{O}_{41})^{-10}$ ; and pH 1.0,  $(\text{Mo}_{24}\text{O}_{78})^{-12}$ . Commercial **ammonium molybdate** has a composition which is approximately  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , but it may not be a definite compound. Lead and the alkaline earth normal molybdates are but slightly soluble, similar to the sulfates and chromates. (Cf. molybdenum orange, **XVII—35**.) The slightly soluble molybdenyl molybdate has been mentioned above.

A compound of analytical importance is the **ammonium phospho-molybdate**,  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ . It forms as a



yellow precipitate, when a solution of ammonium molybdate is added to a solution of orthophosphate in nitric acid. It is readily soluble in ammonia or alkalies and in phosphoric acid, and its solubility is increased in the presence of chloride and many organic acids. Its importance in analytical work lies in its use in separating phosphate from iron and other ions which form slightly soluble phosphates. The composition of the precipitate is approximately as written, but may contain slightly less  $\text{MoO}_3$ , depending on the conditions of precipitation.

Rubidium and thallium phosphomolybdates are likewise insoluble in nitric acid, as are also salts of many of the heavy metals, if the solutions are not too acid. A number of other phosphomolybdate complexes also exist: for example, the compound,  $(\text{NH}_4)_6(\text{PO}_4)_2 \cdot 5\text{MoO}_3 \cdot 7\text{H}_2\text{O}$ , crystallizes from the solution formed by dissolving the ordinary precipitate in excess ammonia.

**22.** Normal molybdates form with hydrogen peroxide the red **peroxy-acid**,  $\text{H}_2\text{MoO}_8$ , and salts of this peroxy-acid have been prepared. With the polymolybdates more complicated peroxy-acids are formed.

The trioxide acts toward strong acids as a basic oxide; with hydrochloric acid it forms the somewhat volatile **oxychloride**,  $\text{MoO}(\text{OH})_2\text{Cl}_2$ ; and with sulfuric acid the **oxysulfate**,  $\text{MoO}_2\text{SO}_4$ . **Oxybrom** compounds also form, but the iodine compounds are not stable. Fluorine forms a **hexahalide**,  $\text{MoF}_6$ , when the metal is heated in the halogen.

Hydrogen sulfide gives with an acid solution of molybdates a precipitate of the **sulfide**,  $\text{MoS}_3$ . This compound is soluble in excess ammonium sulfide with the formation of **thiomolybdate**.

## COMPOUNDS OF TUNGSTEN

**23. Oxidation States.**—Compounds are known containing tungsten with the positive oxidation numbers 2, 3, 4, 5, and 6. The + 6 compounds alone are of importance. In

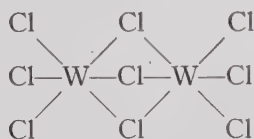


alkaline solution the tungstates (+ 6) are very stable, but tungstic acid in the presence of hydrochloric acid is reduced by stannous chloride to a blue compound, probably  $(\text{WO}_2)_2(\text{WO}_4)$ ; and stronger reducing agents, e.g. tin, will reduce the solution to  $\text{WO}^{+++}$  (green), and upon further action to complex ions of  $\text{W}^{+4}$ , probably  $\text{W}(\text{OH})\text{Cl}_4^-$  (red brown color), and of  $\text{W}^{+3}$ , probably  $\text{W}_2\text{Cl}_9^{---}$  (reddish blue). The following potentials are only approximate and are considerably modified in the presence of halide ions.

	VOLTS <sub>25°</sub>
$\text{W} = \text{W}^{+++} + 3e^-$ .....	< 0.05
$\text{W}^{+++} + 2\text{H}_2\text{O} = \text{WO}_2 + 4\text{H}^+ + e^-$ .....	> 0.05
$2\text{WO}_2 + \text{H}_2\text{O} = \text{W}_2\text{O}_5 + 2\text{H}^+ + 2e^-$ .....	0.0
$\text{W}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{WO}_3 + 2\text{H}^+ + 2e^-$ .....	- 0.15
$\text{WOCl}_4^- + \text{H}_2\text{O} = \text{WO}_2\text{Cl}_3^- + \text{Cl}^- + 2\text{H}^+ + e^-$ .....	- 0.26

**24. The + 2 Compounds.**—The halides,  $\text{WCl}_2$ ,  $\text{WBr}_2$ ,  $\text{WI}_2$ , have been prepared by the action of reducing agents upon higher halides at high temperatures. The chloride is somewhat soluble in water, but the solution hydrolyzes to some complex substance; the compound  $\text{HW}_3\text{Cl}_7 \cdot 4\frac{1}{2}\text{H}_2\text{O}$  has been obtained from alcoholic solutions.

**25. The + 3 Compounds.**—Alkali and ammonia salts, of the general formula,  $\text{R}_3\text{W}_2\text{Cl}_9$ , have been prepared by the reduction of tungstic acid with tin, but no simple compounds of this valence are known. Crystal structure data indicate that the ion  $(\text{W}_2\text{Cl}_9)^{-3}$  has an interesting structure. Six chloride ions form an octahedron about the tungsten as indicated in the following diagram:



**26. The + 4 Compounds.**—The dioxide,  $\text{WO}_2$ , is formed by heating the trioxide in hydrogen, but if too high a temperature is employed the oxide is reduced to the metal.

The oxide is also a product of the hydrolysis of the tetrachloride, or of tetravalent solutions. It is readily oxidized, and with alkali evolves hydrogen and forms tungstate. It is only slightly soluble in acids. Anhydrous **tetrachloride** and **iodide** may be prepared at high temperatures, but they are readily hydrolyzed by water. The **complex cyanide** ion,  $W(CN)_8^{-4}$ , is stable in water solution, and many of its salts have been prepared. The **sulfide**,  $WS_2$ , forms when the trisulfide is ignited. The compound is not soluble in water or dilute hydrogen ion.

**27. The + 5 Compounds.**—The **chloride**,  $WCl_5$ , and **bromide**,  $WBr_5$ , are formed by carefully reducing the hexahalides in hydrogen. The compounds are readily soluble in water, forming light green solutions which contain the ions  $WO^{+++}$  or  $WO_2^+$ ; with excess halide the solution appears to form **complex halides** such as  $WOCl_5^{--}$ .

Similar solutions are formed by the cathodic reduction, or reduction by tin of alcoholic solutions of tungstic acid in hydrochloric acid. When oxalic acid is used, **complex oxalates** are formed, e.g.  $Na_3WO_2(C_2O_4)_2$ . Compounds of the complex cyanide ion  $W(CN)_8^{-3}$  are known.

The addition of ammonia to solutions of the complex chlorides precipitates the hydroxide  $W(OH)_5$ . The sulfide is not known.

Stannous chloride gives with tungstic acid a blue precipitate, **tungsten blue**, which probably has the composition  $(WO_2)_2WO_4$ .

**28. The + 6 Compounds.**—The yellow trioxide,  $WO_3$ , occurs as the mineral wolframocher. It is readily prepared by gently igniting the acid, which is obtained from its salts by digestion with hydrochloric acid. In the cold, the hydrated acid,  $H_2WO_4 \cdot H_2O$ , separates, while in hot solutions, the anhydrous acid precipitates. The former is somewhat soluble in water, but the latter neither dissolves in water nor any acid, except hydrofluoric.

The trioxide also forms many **polytungstates**. Thus,

compounds with sodium oxide of the general formula  $(\text{Na}_2\text{O})_n(\text{WO}_3)_m$  are known, in which, when  $n = 1$ ,  $m$  may vary from 1 to 6; and more complicated compounds in which both  $n$  and  $m$  are large numbers. Except for a few of the alkali compounds, the tungstates are not soluble in water. Although the normal sodium salt,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , is readily prepared, the commercial "tungstate of soda" is the paratungstate,  $\text{Na}_{10}\text{W}_{12}\text{O}_{41} \cdot 28\text{H}_2\text{O}$ . This salt is employed as a mordant in dyeing.

Like molybdenum, the trioxide forms a number of **phosphotungstic** acids. The acid,  $\text{H}_3\text{PO}_4 \cdot 12\text{WO}_3$ , is used as a reagent to precipitate alkaloids and proteins. The oxide also forms **silicotungstic** acids: e.g. by boiling silica with ammonium polytungstate, the compound,  $(\text{NH}_4)_8\text{SiW}_{10}\text{O}_{36} \cdot 8\text{H}_2\text{O}$ , is obtained.

When a solution of sodium paratungstate is boiled with hydrogen peroxide, the solution is found to contain the **peroxytungstate**,  $\text{NaWO}_4 \cdot \text{H}_2\text{O}$ , and many complicated compounds have been obtained.

Tungstates are converted by alkali sulfides into **thiotungstates**, e.g.  $(\text{NH}_4)_2\text{WS}_4$ ; when these solutions are acidified, the **trisulfide**,  $\text{WS}_3$ , is precipitated.

The **hexahalides**,  $\text{WF}_6$ ,  $\text{WCl}_6$ , and  $\text{WBr}_6$  result from the action of the halogens upon the heated metal. The fluoride is also formed by the reaction:  $\text{WCl}_6 + 6\text{HF} = \text{WF}_6 + 6\text{HCl}$ . The **oxyhalides**,  $\text{WO}_2\text{X}_2$  and  $\text{WOX}_4$ , may also be prepared. The fluorides, and also the trioxide, are soluble in excess of fluoride to form complex ions, e.g.  $\text{WO}_2\text{F}_4^{--}$ .

## URANIUM COMPOUNDS

**29. Oxidation States.**—Uranium shows the same numerous oxidation states as the other members of the group, but only the + 4 and + 6 states are stable in aqueous solutions. Thus a trichloride and a pentachloride may be prepared at high temperatures, but the former is oxidized by water with the evolution of hydrogen, and the latter decomposes in

water into compounds of the + 4 and + 6 states. The dioxide is basic and the trioxide is amphoteric, forming with alkalis, uranates, and with acids, uranyl compounds, giving the uranyl ion  $\text{UO}_2^{++}$ . The following oxidation-reduction potentials may be given:

	VOLTS
$\text{U} = \text{UO}_2 + 4\text{H}^+ + 4e^-$ .....	+ 1.4
$\text{UO}_2 = \text{UO}_2^{++} + 2e^-$ .....	- 0.34
$\text{U}^{+++} = \text{U}^{++++} + e^-$ .....	<i>ca.</i> + 0.5

**30. The + 4 Compounds.**—The **hydrated oxide**,  $\text{UO}_2 \cdot 2\text{H}_2\text{O}$ , precipitates when an alkali is added to a uranous solution. The anhydrous oxide may be formed by heating the hydrate, or by reduction of the uranous uranic oxide,  $\text{U}_3\text{O}_8$ , with hydrogen. This oxide is soluble in strong acids forming green solutions of uranous ion. The **tetrafluoride**,  $\text{UF}_4$ , may be precipitated from uranous solution by fluoride ion. The other tetrahalides are soluble, however, and the anhydrous chloride may be prepared along with some of the **pentachloride** by the action of chlorine upon the metal, or  $\text{CCl}_4$  upon  $\text{U}_3\text{O}_4$ . The **sulfide**,  $\text{US}_2$ , forms when the elements are heated together around  $500^\circ$ .

**31. The + 6 Compounds.**—When uranium ores are extracted with a sulfuric nitric acid mixture, the oxide,  $\text{U}_3\text{O}_8$ , is dissolved to form a yellow solution containing **uranyl ion**,  $\text{UO}_2^{++}$ . The **trioxide**,  $\text{UO}_3$ , is difficult to prepare from this solution, as alkalis precipitate alkali uranate. It may, however, be prepared by the decomposition of uranyl nitrate. Upon heating, it forms  $\text{U}_3\text{O}_8$ , and possibly at higher temperatures,  $\text{U}_2\text{O}_5$ .

The uranyl ion forms slightly soluble compounds with phosphates,  $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{UO}_2\text{NH}_4\text{PO}_3$ ; arsenates,  $(\text{UO}_2)_3(\text{AsO}_4)_2$ ; double alkali carbonates,  $\text{UO}_2\text{K}_4(\text{CO}_3)_3$ ; sulfites,  $\text{UO}_2\text{SO}_3 \cdot 4\text{H}_2\text{O}$ ; complex alkali fluorides,  $\text{K}_3\text{UO}_2\text{F}_5$ ; and sulfide,  $\text{UO}_2\text{S}$ . The sulfide is soluble in acid and in ammonium carbonate solution. Uranyl halides, acetate, sulfate, and nitrate are soluble.

Uranyl salts show remarkable fluorescence, and are also subject to photochemical reduction by many organic compounds; for example, uranyl sulfate in sulfuric acid solution is reduced by alcohol in the sunlight to uranous sulfate.

The more common uranates are di-uranates, e.g.,  $K_2U_2O_7$ . They are not soluble in water, but dissolve in acids. The sodium salt, known as uranium yellow, is used in the manufacture of fluorescent uranium glass, and also as a porcelain pigment.

Hydrogen peroxide forms, with uranyl nitrate solution, a precipitate of the **peroxide**,  $UO_4 \cdot 4H_2O$ ; and alkali peroxides form peroxy-uranates, e.g.  $Na_2UO_6 \cdot 4H_2O$ .

**32. Analytical.**—In the systematic separation of the metallic elements, chromium and uranium are associated with the aluminum group in that they are not precipitated by  $H_2S$  in  $0.3N H^+$ , but are precipitated by  $NH_4OH$  and  $(NH_4)_2S$  as  $Cr(OH)_3$  and  $UO_2S$ , respectively. When these precipitates are dissolved in nitric acid and treated with sodium peroxide, the elements remain in solution as  $Na_2CrO_4$  and  $UO_4 \cdot 2Na_2O_2$ . Chromium may be identified by the precipitation of lead chromate from dilute nitric acid solution, and the uranium may be precipitated from a solution of  $UO_2(NO_3)_2$  as  $NH_4UO_2PO_4$ . The ion,  $UO_2^{++}$ , also gives a deep red precipitate with ferrocyanide,  $K_2UO_2 \cdot Fe(CN)_6$ .

Molybdenum resembles antimony in that it is precipitated by  $H_2S$  in  $0.3N H^+$ , and the sulfide is soluble in ammonium sulfide to form the thio-salt. The filtrate from the hydrogen sulfide precipitation, however, is colored blue through the reduction of some of the molybdenum.

In the absence of phosphate, the oxides  $UO_3$  and  $MoO_3$  remain as a residue when their compounds are evaporated with the acids,  $HNO_3 + HClO_4$ , and the product washed with water. These oxides are soluble in hydrogen fluoride, and the hydrated oxide,  $H_2WO_4$ , is not soluble in  $2N HCl$  while  $H_2MoO_4$  is.

Tungstate gives a precipitate of tungsten blue with stannous chloride in dilute HCl; and molybdate gives a precipitate of molybdenum blue with stannous chloride in 12*N* HCl, and an orange color ( $\text{Mo}^{+5}$ ) in dilute acid. The  $\text{Mo}^{+5}$  solution forms, with KCNS, a deep red color of  $\text{MoO}(\text{CNS})_3$ .

In **gravimetric analysis**, the following pure compounds may be separated and weighed:  $\text{Cr}_2\text{O}_3$ ,  $\text{BaCrO}_4$ ,  $\text{MoO}_3$ ,  $\text{PbMoO}_4$ ,  $\text{WO}_3$ , and  $\text{U}_3\text{O}_8$ . The trioxides of molybdenum and tungsten may be separated by precipitating the mercurous salts, which are then ignited to the oxide.

In **volumetric analysis** dichromate may be titrated against ferrous ion, or an excess of iodide may be added to dichromate in acid, and the iodine titrated with thiosulfate.

Molybdates may be reduced to  $\text{MoO}_2^+$  with hydrogen iodide, and the iodine determined with thiosulfate, or the molybdate may be reduced to  $\text{Mo}^{+++}$  by zinc, and the product titrated with permanganate.

Uranates may also be reduced with zinc and the solution of  $\text{UO}_2^{++}$  titrated with permanganate.



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## Chapter XVIII

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### SUBGROUP VII. MANGANESE AND RHENIUM

1. Although manganese is one of the more abundant elements, the other two members of Subgroup VII, masurium and rhenium, but recently discovered, exist in extremely small amounts. Almost our only knowledge of masurium is the presence of lines in the X-ray spectrum of certain platinum and columbium compounds, whose frequencies correspond to those calculated for the element of atomic number 43.

The discussion of the relation of atomic structure and oxidation states of the elements of Subgroup VI is also applicable to Subgroup VII except, of course, that these elements possess one more electron. In the  $+7$  state they show certain resemblances to the perhalates, but in the lower states they are more closely related to the elements of neighboring atomic numbers. These latter relations are further discussed in Chapter XIX. The  $-1$  state of rhenium has been reported. This seems most remarkable, since octet formation is otherwise restricted to s-p electron groups.

2. **Occurrence.**—Manganese is ranked 9th among the metals in order of abundance, the estimated percentage in igneous rocks being 0.10. The principal ore is pyrolusite,  $\text{MnO}_2$ . Other minerals are braunite,  $\text{Mn}_2\text{O}_3$ ; manganite,  $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ; hausmannite,  $\text{Mn}_3\text{O}_4$ ; rhodochrosite,  $\text{MnCO}_3$ ; alabandite,  $\text{MnS}$ ; hauerite,  $\text{MnS}_2$ . The manganese ores are generally associated with iron.

The principal commercial source of rhenium is the copper-bearing slates of Germany where it is present 1 to 5 parts per million. It is concentrated along with the molybdenum present.

**3. The Metals.**—Manganese is difficult to prepare in the pure state by reduction with carbon, as it forms a series of solid solutions with the carbide,  $\text{Mn}_3\text{C}$ . It is generally prepared by the reduction of the oxide by aluminum. However, all of the manganese consumed in the steel industry is utilized in the form of the iron alloys, **spiegel iron** (15–25 per cent Mn) and **ferromanganese** (70–80 per cent Mn), which are prepared by reducing the mixed ores in the blast furnace. About a million tons of manganese ore (containing about 35 per cent Mn) are imported annually by the United States.

The pure metal is reddish-gray, and relatively soft compared to iron, but if it contains carbon, it is very hard and brittle. The melting point is lower than those of either iron or chromium. The metal tarnishes readily in moist air, especially if it contains the carbide,  $\text{Mn}_3\text{C}$ , which evolves methane and hydrogen with water.

The introduction of manganese into steel improves the rolling and forging qualities of the steel and contributes toughness and resistance to wear. It is considered to be the best deoxidizing and desulfurizing agent for steel, this

TABLE I  
ATOMIC AND PHYSICAL PROPERTIES OF ELEMENTS OF SUBGROUP VII

	Mn	Ma	Re
Atomic weight.....	54.93	98–99	186.31
Atomic number.....	25	43	75
Isotopes.....	55	—	185, 187
Density.....	7.2	—	21.4
Melting point, ° C.....	1220	—	3440
Boiling point, ° C.....	2150	—	—
Electrical resistivity, ohm-cm. ....	$5 \times 10^{-6}$	—	$2 \times 10^{-5}$
Ionization potential of gas atom, volts.....	7.4	—	—

property depending, in part, upon the very slight solubility of the manganous oxide and sulfide in molten iron.

**Manganese bronze** contains about 30 per cent manganese in copper. The alloy **manganin** (Cu 84, Mn 12, Ni 4) has a very low temperature coefficient of resistance and is used in electrical instruments.

Rhenium metal may be prepared by electrolytic precipitation from water solution of the perrhenate. In contact with water it is readily oxidized back to the perrhenate. The metal is somewhat soft and ductile. There are no commercial uses at present.

TABLE II

## REACTIONS OF MANGANESE

$3\text{Mn} + 2\text{O}_2 = \text{Mn}_3\text{O}_4$	Heated in air
$\text{Mn} + 2\text{H}^+ = \text{Mn}^{++} + \text{H}_2$	
$\text{Mn} + 2\text{H}_2\text{O} = \text{Mn}(\text{OH})_2 + \text{H}_2$	Slowly in cold
$\text{Mn} + \text{X}_2 = \text{MnX}_2$	X = halogen. $\text{F}_2$ also gives $\text{MnF}_3$
$\text{Mn} + \text{S} = \text{MnS}$	Heated together
$3\text{Mn} + \text{C} = \text{Mn}_3\text{C}$	High temperature. With Si forms $\text{MnSi}$ and $\text{Mn}_2\text{Si}$
$10\text{Mn} + 3\text{N}_2 = 2\text{Mn}_5\text{N}_3$	Burns in $\text{N}_2$ at $1200^\circ$ . With P forms $\text{Mn}_5\text{P}_2$ and $\text{MnP}$
$2\text{Mn} + 4\text{KOH} + 3\text{O}_2 = 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$	

**4. Reactions of the Metals.**—The electropositive nature (Par. 5) of manganese renders it highly reactive toward oxidizing agents. The principal reactions are given in Table II. Rhenium is less electropositive than manganese and is not oxidized as readily by weak oxidizing agents, but moderately strong oxidizing agents will carry it all the way up to the perrhenate. By direct reaction with the elements metallic rhenium forms  $\text{Re}_2\text{O}_7$ ,  $\text{ReF}_6$ ,  $\text{ReCl}_4$ ,  $\text{ReBr}_3$ , and  $\text{ReS}_2$ .

## COMPOUNDS OF MANGANESE

**5. Oxidation States.**—Manganese forms compounds having the positive oxidation states 2, 3, 4, 6, and 7. The two lower states are basic, the +4 amphoteric, and the two

higher states acidic. There is evidence for the + 1 complex cyanide, e.g.  $\text{K}_5\text{Mn}(\text{CN})_6$ . The oxidation-reduction potentials relating to the various states are summarized below:

	VOLTS
$\text{Mn} = \text{Mn}^{++} + 2e^-$ .....	+ 1.05
$\text{Mn}^{++} + 2\text{H}_2\text{O} = \text{MnO}_2 + 4\text{H}^+ + 2e^-$ .....	- 1.28 ✓
$\text{Mn}^{++} = \text{Mn}^{+++} + e^-$ .....	- 1.5 ✓
$\text{Mn}^{+++} + 2\text{H}_2\text{O} = \text{MnO}_2 + 4\text{H}^+ + e^-$ .....	- 1.1
$\text{MnO}_2 + 4\text{OH}^- = \text{MnO}_4^{--} + 2\text{H}_2\text{O} + 2e^-$ .....	- 0.58 ✓
$\text{MnO}_2 + 2\text{H}_2\text{O} = \text{MnO}_4^- + 4\text{H}^+ + 3e^-$ .....	- 1.67 ✓
$\text{MnO}_2 + 4\text{OH}^- = \text{MnO}_4^- + 2\text{H}_2\text{O} + 3e^-$ .....	- 0.57 ✓
$\text{Mn}^{++} + 4\text{H}_2\text{O} = \text{MnO}_4^- + 8\text{H}^+ + 5e^-$ .....	- 1.52 ✓
$\text{MnO}_4^{--} = \text{MnO}_4^- + e^-$ .....	- 0.54 ✓

A number of very important relations in the chemistry of manganese may be correlated with these values:

Manganic ion,  $\text{Mn}^{+++}$ , is unstable even at very low concentrations in respect to the decomposition:  $2\text{Mn}^{+++} + 2\text{H}_2\text{O} = \text{Mn}^{++} + \text{MnO}_2 + 4\text{H}^+$ .

Manganate,  $\text{MnO}_4^{--}$ , when acidified, decomposes to the dioxide and permanganate:  $3\text{MnO}_4^{--} + 4\text{H}^+ = \text{MnO}_2 + 2\text{MnO}_4^- + 2\text{H}_2\text{O}$ .

Permanganate in acid solution will oxidize manganous ion to the dioxide, and in alkaline solution will oxidize the dioxide to manganate.

Manganese dioxide in concentrated acid, and permanganate in both concentrated acid and alkali, will slowly evolve oxygen from water. (See Oxidation-reduction Potential of Oxygen.)

Oxygen in normal alkali is not capable of oxidizing the dioxide to manganate, but the reaction does occur in fused potassium hydroxide.

Excess of a reducing agent upon permanganate in acid solution yields manganous ion; but in alkaline or neutral solution the product is the dioxide. Partial reduction of permanganate in alkaline solution gives manganate, but excess of reducing agent gives the dioxide.

**6. Manganous Ion.**—Compounds of the + 2 state are known as manganous. They resemble magnesium and ferrous iron in their solubility relations, and are in general characterized by a delicate pink color. The **hydroxide**,  $\text{Mn}(\text{OH})_2$ , forms when alkali or ammonium hydroxides are added to a manganous solution. Like magnesium hydroxide, it is soluble in ammonium salts. In the air, it quickly darkens through the oxidation to manganic hydroxide,  $\text{Mn}(\text{OH})_3$ , or possibly  $\text{MnO} \cdot \text{MnO}_2 \cdot n\text{H}_2\text{O}$ . When heated in the absence of air, the hydroxide forms the **oxide**,  $\text{MnO}$ ; and this, heated in air, is oxidized to  $\text{Mn}_3\text{O}_4$ .

Alkali and ammonium carbonates precipitate the **carbonate**,  $\text{MnCO}_3$ . This, like the hydroxide, is soluble in excess ammonium ion.

The pink **sulfide**,  $\text{MnS}$ , though precipitated by soluble sulfides, is readily soluble in dilute acids. The moist solid oxidizes, upon standing in the air, to the sulfate.

The **sulfate**, **nitrate**, **halides**, and **cyanide** are soluble; and the last forms the complex ions  $\text{Mn}(\text{CN})_3^-$  and  $\text{Mn}(\text{CN})_6^{4-}$ . The sulfate crystallizes in a number of hydrated forms, a transition from the penta-hydrate to the tetra-hydrate occurring at about  $26^\circ$ . It forms double salts, such as  $\text{K}_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot 6\text{H}_2\text{O}$ , isomorphous with the corresponding salts of magnesium.

The **ammonium phosphate**,  $\text{NH}_4\text{MnPO}_4$ , **ferrocyanide**,  $\text{Mn}_2\text{Fe}(\text{CN})_6$ , and **oxalate**,  $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , are but slightly soluble, and are of importance in analytical work.

**7. Manganese in the + 3 State.**—Reference has been made in the preceding paragraph to the formation of the **hydroxide**,  $\text{Mn}(\text{OH})_3$  (probably hydrous oxide), by oxidation of manganous hydroxide. Due to the instability of the manganic ion,  $\text{Mn}^{+++}$  (Par. 5), the only compounds which can be prepared from water solutions are slightly soluble, or slightly dissociated.

The **trifluoride** may be prepared by the action of fluorine upon the metal, and the **trichloride** by the decomposition

of the tetrachloride. In water, they decompose, e.g.  $2\text{MnF}_3 + 2\text{H}_2\text{O} = \text{Mn}^{++} + 6\text{F}^- + \text{MnO}_2 + 4\text{H}^+$ , but a deep red solution containing the complex fluoride,  $\text{K}_2\text{MnF}_6$ , may be prepared by dissolving the hydroxide in excess of potassium acid fluoride. There is evidence of the formation of some  $\text{H}_2\text{MnCl}_5$  when the dioxide is treated with concentrated hydrochloric acid. Powerful oxidizing agents in concentrated hydrochloric acid oxidize manganous ion to the complex chloride. The hydroxide in sulfuric acid forms an unstable **sulfate**, and **alums** have been prepared. Powerful oxidizing agents, e.g.  $\text{KMnO}_4$ , convert manganous ion, in excess acetic acid, into manganic **acetate**.

**8. Manganese Dioxide.**—The chemistry of + 4 manganese deals largely with the **dioxide**,  $\text{MnO}_2$ . As the mineral, pyrolusite, it is the most important source of the element. In many respects, the dioxide resembles lead dioxide; and like the latter, although essentially amphoteric, it is comparatively inert toward both acids and bases. In cold concentrated hydrochloric acid, the oxide dissolves slowly to form a green solution of the **tetrachloride**, and the hydrous dioxide may be reprecipitated from this solution; but upon heating, chlorine is evolved and manganous chloride formed. The sulfate may also be obtained in solution, but it is very unstable toward the evolution of oxygen. A **complex fluoride**,  $\text{K}_2\text{MnF}_6$ , however, is more stable.

The oxide does not dissolve readily in alkali, but **manganites** are formed by fusing the oxide with certain basic oxides. Calcium manganite,  $\text{CaMn}_2\text{O}_5$ , is prepared by oxidizing manganous oxide with bleaching powder, and potassium manganite,  $\text{K}_2\text{Mn}_5\text{O}_{11}$ , by passing carbon dioxide into potassium manganate solution. The oxides,  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$ , may be considered as manganous manganites; upon heating, the dioxide loses oxygen to form these oxides or possibly solid solutions of the type  $(\text{MnO})_n(\text{MnO}_2)_m$ .

The oxidation-reduction potentials of the dioxide have been discussed in Paragraph 5.



Manganese dioxide is employed in the paint and varnish industry to catalyze the oxidation of oils by oxygen, i.e. the drying process. The glass industry employs the dioxide to neutralize the green color of ferrous silicate impurities. The largest use (about 30,000 tons in U. S. annually) of the dioxide is as the oxidizing constituent of the ordinary dry cell.

**9. "Dry Cells."**—The dry Leclanché battery, generally called the "dry cell," consists of a zinc anode, a cathode of carbon packed in manganese dioxide, and an electrolyte of ammonium chloride solution, containing a little zinc chloride, which is held in a porous solid (kieselguhr). The anode reaction is  $\text{Zn} + 2\text{Cl}^- = \text{ZnCl}_2(\text{s}) + 2\text{e}^-$ ; and the cathode reaction,  $\text{MnO}_2 + \text{NH}_4^+ + 2\text{H}_2\text{O} + \text{e}^- = \text{NH}_4\text{OH} + \text{Mn}(\text{OH})_3$ . The voltage is 1.48. Large currents cannot be drawn from the cell, owing to the polarization of the cathode, possibly due to the slow diffusion of the electrolyte.

**10. Manganate.**—When manganese dioxide is fused with potassium hydroxide, some decomposition occurs:  $3\text{MnO}_2 + 2\text{KOH} = \text{Mn}_2\text{O}_3 + \text{K}_2\text{MnO}_4 + \text{H}_2\text{O}$ . In the presence of air or other oxidizing agents, as potassium chlorate, the manganese is all oxidized to manganate:  $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 = 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$ . The potassium compound is soluble in water, giving a green solution, from which the salt may be crystallized. Manganates are somewhat similar in solubility to sulfates. The free acid cannot be prepared because of the decomposition into the dioxide and permanganate:  $3\text{MnO}_4^{--} + 4\text{H}^+ = \text{MnO}_2 + 2\text{MnO}_4^- + 2\text{H}_2\text{O}$ ; but the very unstable trioxide has been prepared by the reaction:  $(\text{MnO}_3)_2\text{SO}_4 + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{SO}_4 + 2\text{MnO}_3 + \text{CO}_2 + \frac{1}{2}\text{O}_2$ . Reference should be made to Paragraph 5 for the oxidation-reduction relations of manganate.

**11. Permanganate.**—When the concentration of hydroxide in a manganate solution is decreased, the color changes from green to purple with the formation of permanganate

and the dioxide:  $3\text{MnO}_4^{--} + 2\text{H}_2\text{O} = 2\text{MnO}_4^- + \text{MnO}_2 + 4\text{OH}^-$ . The conversion of manganate into permanganate may also be carried out by powerful oxidizing agents in alkaline solution: e.g.  $2\text{MnO}_4^{--} + \text{ClO}^- + \text{H}_2\text{O} = 2\text{MnO}_4^- + \text{Cl}^- + 2\text{OH}^-$ .

A solution of **permanganic acid**,  $\text{HMnO}_4$ , may be prepared by the reaction of dilute sulfuric acid and barium permanganate, or by the oxidation of manganous sulfate by lead dioxide:  $2\text{MnSO}_4 + 5\text{PbO}_2 + 3\text{H}_2\text{SO}_4 = 2\text{HMnO}_4 + 5\text{PbSO}_4 + 2\text{H}_2\text{O}$ . The solution decomposes upon boiling, or in the sunlight. When potassium permanganate is treated with cold concentrated sulfuric acid, the solution turns green through the formation of the sulfate,  $(\text{MnO}_3)_2\text{SO}_4$ ; and upon the careful addition of cold water, the **heptoxide**,  $\text{Mn}_2\text{O}_7$ , separates as a dark brown, highly explosive liquid.

**Alkali permanganates** are usually prepared commercially by fusing the dioxide with alkali hydroxide in air to form the manganate, followed by oxidation with chlorine in the alkaline solution. They may also be prepared by the anodic oxidation of manganate.

If a pure permanganate is desired, the potassium salt is generally employed instead of the sodium salt, as the great solubility of the latter renders it difficult to prepare free from impurities. Alkali permanganates are used as disinfectants (Condy's Liquid), as oxidizing agents in industrial processes, and as volumetric reagents (Par. 15).

## COMPOUNDS OF RHENIUM

**12. Oxidation States.**—Rhenium forms the oxides  $\text{Re}_2\text{O}_3$ ,  $\text{ReO}_2$ ,  $\text{ReO}_3$ ,  $\text{Re}_2\text{O}_7$  and claims have been made for the formation of  $\text{Re}_2\text{O}$ . Halides or complex halides are known corresponding to the oxidation states + 3, + 4, + 5, + 6, and + 7. When perrhenate is reduced in acid solution with zinc, eight equivalents of oxidizing agent are required to oxidize the solution, and this constitutes evidence for the

existence of rhenide ion,  $\text{Re}^-$ . The following potentials are only approximate:

	VOLTS $25^\circ$
$\text{Re} + \text{H}_2\text{O} = \text{ReO}_4^- + 8\text{H}^+ + 7e^-$ .....	- 0.15
$\text{Re} + 2\text{H}_2\text{O} = \text{ReO}_2 + 4\text{H}^+ + 4e^-$ .....	ca. 0.0
$\text{ReCl}_6^{--} + 4\text{H}_2\text{O} = \text{ReO}_4^- + 6\text{Cl}^- + 8\text{H}^+ + 3e^-$ .....	ca. - 0.5
$\text{Re} + 4\text{Cl}^- = \text{ReCl}_4^- + 3e^-$ .....	> 0.1
$\text{Re}^- = \text{Re} + e^-$ .....	ca. 0.4

**13. Perrhenate.**—The oxide,  $\text{Re}_2\text{O}_7$ , is colorless and dissolves readily in water to give the solution of **perrhenic acid**,  $\text{HReO}_4$ . The potassium, silver, and thallos salts are but slightly soluble. So-called “mesoperrhenates,” e.g.  $\text{Ba}_3(\text{ReO}_5)_2$ , are formed with excess base. The acid is a poor oxidizing agent (Par. 12) but in the presence of hydrochloric acid it is somewhat more powerful because of the formation of the complex ion  $\text{ReCl}_6^{--}$ , and will oxidize iodide. The sulfide,  $\text{Re}_2\text{S}_7$ , is precipitated by  $\text{H}_2\text{S}$  in ammonia solution and is soluble in excess sulfide with the formation of thio-perrhenate,  $\text{ReS}_4^-$ .

**14. The Lower Oxidation States.**—The complex chloride ions,  $\text{ReCl}_4^-$  and  $\text{ReCl}_6^{--}$ , may be prepared by the reduction of perrhenate in hydrochloric acid and a + 5 complex stable in high chloride has been reported although the compound  $\text{ReCl}_5$  is said to decompose in water into  $\text{ReO}_4^-$  and  $\text{ReCl}_6^{--}$ . The trioxide is soluble in hydroxide, but the solution is unstable with respect to decomposition into  $\text{ReO}_4$  and  $\text{ReO}_2$ . However, the barium rhenate,  $\text{BaReO}_4$ , has been described. The dioxide is amphoteric but somewhat inert to both acids and bases. The hyrous sesquioxide is precipitated by hydrolysis of the trichloride. The sulfide,  $\text{ReS}_2$ , is formed when  $\text{Re}_2\text{S}_7$  is heated. The highest fluoride which has been reported is  $\text{ReF}_6$ . The compounds  $\text{K}_2\text{ReF}_6 \cdot \text{ReOF}_4$ , and  $\text{ReO}_2\text{F}_2$  have been prepared.

**15. Analytical.**—Potassium permanganate is the most widely used oxidizing agent in volumetric analysis. Its importance depends upon its ability to oxidize quantitatively

a very large number of substances. These include the direct oxidation to a higher oxidation state of ions or compounds of  $\text{Fe}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Cu}^+$ ,  $\text{Sn}^{++}$ ,  $\text{As}^{+++}$ ,  $\text{Sb}^{+++}$ ,  $\text{Ti}^{+++}$ ,  $\text{Mo}^{+3}$ ,  $\text{W}^{+5}$ ,  $\text{U}^{+4}$ , and  $\text{V}^{+4}$ ; the oxidation of the inorganic acids  $\text{HNO}_2$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{HCNS}$ ; the oxidation of organic acids or their salts, such as oxalic and formic acids. In addition to these determinations by direct oxidation, many methods of indirect determinations have been worked out, such as the precipitation of Ca, Sr, Ba, Cu, Pb, Zn, Hg (ous), Ce, and La as oxalates, and the subsequent oxidation of the oxalic acid; the determination of phosphate by the precipitation of  $(\text{NH}_3)_3\text{PO}_4 \cdot 12\text{MoO}_3$ , and the subsequent reduction of the  $\text{MoO}_3$  to  $\text{Mo}^{+++}$  and reoxidation; the determination of potassium by precipitation with cobalt nitrite and the oxidation of the nitrite; and the standardization of  $\text{Na}_2\text{S}_2\text{O}_3$  solution by the addition of a known weight of  $\text{KMnO}_4$  to excess  $\text{I}^-$ , followed by the titration of the  $\text{I}_2$  liberated by the thiosulfate. Powerful oxidizing agents, e.g.  $\text{PbO}_2$  may be determined by the addition of a known excess of a reducing agent, e.g.  $\text{Fe}^{++}$  and its titration by permanganate.

In acid solution, permanganate is reduced to manganous ion:  $\text{MnO}_4^- + 8\text{H}^+ + 5e^- = \text{Mn}^{++} + 4\text{H}_2\text{O}$ . Since 5 equivalents of electricity are involved, a one normal (one equivalent of oxidizing power) solution of permanganate is defined as 1/5 molal, when it is to be employed in the above reaction. Commercial potassium permanganate is not of sufficient purity to permit standardization by directly weighing out the salt; hence the solution is generally standardized in terms of one of the following primary standards: sodium oxalate, oxalic acid, pure iron, or ferrous ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ .

One of the advantages of permanganate is that the distinct color change of the reaction serves as an endpoint indicator. However, care must be taken in titrating a reducing agent with permanganate not to approach the end-

point too rapidly, as excess of the reagent may react with manganous ion to form compounds of  $Mn^{+3}$  or  $Mn^{+4}$ , which might not be completely reduced.

In alkaline or neutral solutions, permanganate is reduced to the dioxide:  $MnO_4^- + 2H_2O + 3e^- = MnO_2 + 4OH^-$ ; hence a normal solution of permanganate for use under these conditions is defined as 1/3 molal. One of the important applications of this reaction is in the titration of manganous salts in neutral solution:  $3Mn^{++} + 2MnO_4^- + 2H_2O = 5MnO_2 + 4H^+$ .

In the gravimetric determination of manganese, it may be precipitated as the ammonium manganese phosphate, and ignited to the pyrophosphate. Manganous compounds may also be precipitated as the dioxide by strong oxidizing agents, bromine water frequently being employed. Upon ignition, the dioxide yields  $Mn_3O_4$ . Gravimetric determination may also be carried out with the manganous carbonate and sulfide.

In the systematic scheme of qualitative analysis, manganese is associated with the group thrown down by ammonium sulfide (Append. VI). A very delicate confirmatory test is the formation of a purple permanganate color when a very small concentration of manganous is boiled with lead dioxide and concentrated nitric acid.

Rhenium is precipitated as the sulfide in acid solution and like stannic sulfide is soluble in excess of sulfide. The element may be determined by precipitation of the slightly soluble  $AgReO_4$  or  $TlReO_4$ , and also by precipitation with 8-hydroxyquinoline.

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# Chapter XIX

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## IRON, COBALT, AND NICKEL

1. The first "transition series," in which the electrons in the third quantum state (Append. XVIII) are being increased from 8 to 18, is complete with copper; and the three preceding elements, iron, cobalt, and nickel, constitute a triad possessing many common properties, as might be expected from the fact that the differences in behavior are due merely to the number of  $d$  electrons.

The free elements are metals of similar appearance, melting point, density, and other physical properties. They show marked resemblance to all the members of the transition series, although a gradual change in properties may be noted between titanium and nickel (Table I).

The three metals are readily oxidized to the  $+2$  state, but the removal of an additional electron to form the  $+3$  ion becomes increasingly difficult with increasing atomic number: thus, ferric ion is a good oxidizing agent; cobaltic ion a very powerful oxidizing agent; and nickelic ion is not known. The  $+2$  ions are similar in properties to the corresponding ions of other elements of the series, especially the adjacent elements, as has been pointed out under chromium and manganese.

Powerful oxidizing agents acting in alkaline solution form salts in which the elements are in the  $+4$  state, or, in the case of iron, the  $+6$  state. These are the highest states shown by the group and in this respect they are intermediate to chromium and manganese, on the one hand, in which



TABLE I  
FIRST TRANSITION SERIES

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Melting point..	1800	1710	1550	1220	1530	1490	1452	1084	419
Density..	4.5	5.9	7.1	7.2	7.9	8.9	8.9	8.9	7.1
Oxidation states.	(2),3,4	3,4,5	2,3,6	2,4,6,7	2,3,(6)	2, 3	2, 4	1, 2	2
Oxides..	—	—	—	—	—	—	Ni <sub>2</sub> O?	Cu <sub>2</sub> O	—
	TiO	VO	CrO	MnO	FeO	CoO	NiO	CuO	ZnO
	Ti <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub> *	Fe <sub>2</sub> O <sub>3</sub>	Co <sub>2</sub> O <sub>3</sub>	Ni <sub>2</sub> O <sub>3</sub> *	Cu <sub>2</sub> O <sub>3</sub>	—
	—	—	—	Mn <sub>3</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub>	Co <sub>3</sub> O <sub>4</sub>	Ni <sub>3</sub> O <sub>4</sub>	—	—
	TiO <sub>2</sub>	VO <sub>2</sub>	CrO <sub>2</sub> *	MnO <sub>2</sub>	FeO <sub>2</sub> †	CoO <sub>2</sub>	NiO <sub>2</sub>	—	—
	—	V <sub>2</sub> O <sub>5</sub>	—	—	—	—	—	—	—
	—	—	CrO <sub>3</sub>	MnO <sub>3</sub>	FeO <sub>3</sub> †	—	—	—	—
	—	—	—	Mn <sub>2</sub> O <sub>7</sub>	—	—	—	—	—
Ionization potential...	6.81	6.71	6.74	7.41	7.83	7.81	7.61	7.68	9.36

\* This oxide may be a mixture of higher and lower oxides.

† Oxide known only in compounds.

all of the "transition" electrons may be removed, e.g. in chromate and permanganate, and to copper and zinc, on the other hand, in which one and none, respectively, of the electrons of the 18 group may be readily removed. These relations are further summarized in Table I.

Another important characteristic of iron, cobalt, and nickel is the tendency to form complex ions. This property has been discussed in Chapter VII as related to the very high fields of force existing about the "18 electron kernel" type of ion, and since these transition elements are approaching to this structure, it is not surprising that they also possess this property to a high degree.

A number of relations between iron, cobalt, and nickel, and the corresponding members of the second and third transition series, are discussed in connection with these elements, Chapter XX, but in general the "horizontal"

periodic relations are more marked than the "vertical," e.g., iron resembles cobalt more than it does ruthenium.

## IRON

**2. Occurrence.**—The average percentage of iron in the igneous rocks is given as 5.01. The percentage is doubtless higher in the low lying basaltic rocks, and the central core of the earth (diameter about 2,500 miles) is largely iron. The metallic meteors are generally over 90 per cent iron. Among the elements of the earth's crust (outer ten miles) iron ranks only fourth in abundance.

The free metal is rarely found on the earth's surface, and then the specimen is generally of meteoric origin. Igneous rocks contain ferrous silicates isomorphous with magnesium silicates as  $[\text{Mg}, \text{Fe}]\text{SiO}_4$  (cf. **XIV**—Table VI); ferric alumino-silicates as orthoclase,  $\text{K}[\text{Al}, \text{Fe}]\text{Si}_3\text{O}_8$ ; and numerous sulfides, the more important being pyrrhotite,  $\text{FeS}(\text{S})_x$ , and pyrites,  $\text{FeS}_2$ .

The weathering of the igneous rocks has resulted in the formation of deposits of oxides and carbonates which are the commercial source of the metal. The principal ores are: hematite,  $\text{Fe}_2\text{O}_3$ ; brown ore,  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ , including limonite,  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ; magnetite,  $\text{Fe}_3\text{O}_4$ ; and siderite, spathic iron or "kidney ore,"  $\text{FeCO}_3$ .

In addition to the above, hundreds of minerals are known containing iron in combination with practically all of the acid oxides, and with the sulfides and compounds of other positive elements. Iron is also an essential constituent of the haemoglobin of the blood.

**3. Pure Iron.**—Iron is tetramorphous; the transition temperatures between the forms are given in Table II. **A-iron**, called **ferrite**, is a soft, tough, grey-white metal. The crystal lattice is the body-centered cubic type; the metal is highly paramagnetic. The transition from  $\alpha$ - to  $\beta$ -**iron** does not involve a change in the lattice structure, and appears to be

largely electronic in nature, as the unusually high magnetic permeability of  $\alpha$ -iron disappears in  $\beta$ -iron. The total energy absorbed in the transition is small, and the change appears to start many degrees below the recorded transition point.

TABLE II  
ATOMIC AND PHYSICAL PROPERTIES OF IRON

Atomic weight.....	55.84	Density, 20° C.....	7.86
Atomic number.....	26	Electrical resistivity,	
Isotopes.....	54, 56, 57, 58	ohm-cm.....	$10.0 \times 10^{-6}$
Electrons in various		Size of the Fe <sup>++</sup> ion,	
quantum levels, 1st....	2	cm. $\times 10^8$ .....	0.75
2d....	8	Ionization potential of	
3d....	8 + 6	gas atom, volts.....	7.83
4th....	2	Tensile strength in lbs.	
Boiling point, ° C.....	2735	per sq. in.:	
Melting point, ° C.....	1530	Iron, cast.....	13,000–33,000
Transition temperatures:		Iron, drawn.....	50,000–100,000
$\alpha$ to $\beta$ .....	766	Steel.....	40,000–300,000
$\beta$ to $\gamma$ .....	895		
$\gamma$ to $\delta$ .....	1400		

**$\Gamma$ -iron** is but slightly magnetic in comparison to the  $\alpha$ -form. Its lattice structure is face-centered cubic.  $\Gamma$ -iron forms solid solutions with iron carbide, and these may be obtained at room temperature in a metastable state by rapid quenching. The importance of this fact is discussed under Steel. Little is known regarding the properties of  **$\delta$ -iron**.

Pure iron is of only slight commercial importance. It may be prepared by heating the oxide in a current of hydrogen, and by the electrolysis of ferrous sulfate solution. In both of these preparations, the iron contains absorbed hydrogen which may be removed by heating in a vacuum. The hydrogen appears to dissolve to form a true solution; the same is true of nitrogen and other gases at higher temperatures.

**4. Metallurgy of Pig Iron.**—The basic principle involved in the smelting of iron is the reduction of the iron oxides by

carbon monoxide. At a comparatively low temperature, ferric oxide is converted completely to the magnetic oxide:  $3\text{Fe}_2\text{O}_3 + \text{CO} = 2\text{Fe}_3\text{O}_4 + \text{CO}_2$ . At higher temperatures this oxide is reduced to ferrous oxide, and then to the metal, but these reactions involve measurable equilibria and are reversible, depending upon the relative pressures of carbon monoxide and dioxide.

TABLE III  
REACTIONS OF CARBON MONOXIDE AND OXIDES OF IRON  
Values for the ratio  $\text{CO}_2/\text{CO}$  at various temperatures

REACTION	TEMPERATURE, ° C.			
	700	800	900	1,000
$\text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2$ .....	0.68	0.55	0.47	0.40
$\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$ .....	1.68	2.40	3.24	4.17

The modern blast furnace operates so as to carry out these reactions in a continuous manner. The general outline of this furnace is indicated in Fig. 1. The dimensions are approximately 22 by 90 ft., and the construction is sheet steel lined with difficultly fusible siliceous fire brick. Only ores with low sulfur and phosphorus content are employed, and these may be subjected to a preliminary roasting in order to remove as much sulfur as possible. The ore contains siliceous material, and as all the charge is to be drawn from the furnace in the liquid state, sufficient limestone is added to form an easily fusible calcium silicate slag. Coke is now universally employed as fuel, and is introduced together with the ore and limestone at the top of the furnace.

Dry air, preheated to 425 to 650°, is blown in through a number of water jacketed nozzles or tuyeres near the bottom. The air oxidizes the coke in the lower part of the furnace to carbon monoxide (cf. XIII—6). The intense heat of this reaction liquefies the iron which has been reduced in the central part of the furnace by the hot carbon monoxide.

From time to time, the molten metal is drawn off, and

either run into molds, or else conveyed directly to Bessemer converters, or open hearth furnaces, and made into steel. The crude iron is called cast iron, or "**pig iron**," from the shape of the casts made in the old-fashioned furnaces. The impurities present depend considerably upon the composition of the ore, the nature of the slag, and the temperature at which the furnace has been maintained. The following percentages are representative: C, 2–4.5; Si, 0.7–3; S, 0.1–0.3; P, 0.–3.0; Mn, 0.2–1. In general, a high temperature of reduction increases the percentage of carbon and silicon, but diminishes that of the sulfur through the reaction:  $\text{FeS} + \text{CaO} + \text{CO} = \text{Fe} + \text{CaS} + \text{CO}_2$ . Practically all of the phosphorus in the charge collects in the iron as  $\text{Fe}_3\text{P}$ .

The world production of pig iron in 1937 was about 100 million tons, of which approximately 40 per cent was made in the United States. The melting point of pig iron is about  $1150^\circ$ . The metal is brittle and suitable only for castings not subject to shock. When cooled rapidly, the carbon remains in combination and the product is called **white cast iron**; but when

cooled slowly, much of the carbon separates as graphite and the product, known as **grey cast iron**, is softer and tougher.

**Blast furnace slag** has the approximate percentage composition:  $\text{SiO}_2$ , 20–70; CaO and MgO, 25–50;  $\text{Al}_2\text{O}_3$ , 5–20;

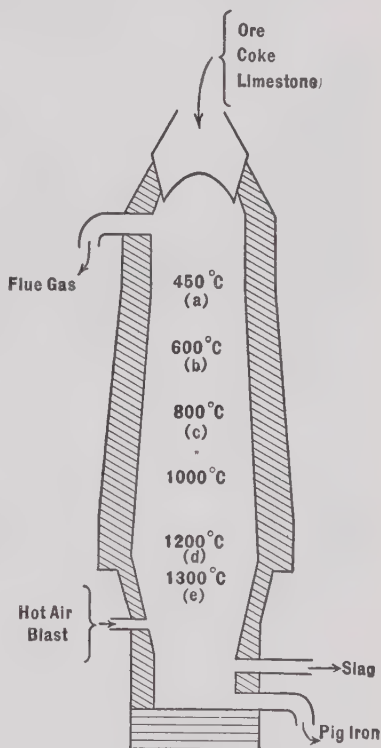


FIG. 1. Blast furnace (diagrammatic).

CaS, 1-4; FeO, 1. In some cases, the composition is such that the slag may be ground and made into cement. Large quantities are also used in paving, in combination with tar.

The **flue gas** contains considerable heat value through its high carbon monoxide content. Part of the gas is burned in the so-called hot-blast stoves, which are used to preheat the air blast, and the rest is employed to develop power about the plant. The gas is generally cleaned from dust before using for power, and the solid obtained contains appreciable quantities of potassium salts, and constitutes a potential source of this alkali.

**5. Wrought Iron.**—Wrought iron is manufactured from pig iron by oxidizing out the impurities through melting in a reverberatory furnace with iron oxide and a basic flux. As the iron becomes pure, its melting point rises, and the metal collects in lumps which are removed from the furnace. Wrought iron is soft and malleable. It possesses a fibrous structure due to the inclusion of slag, since the temperature

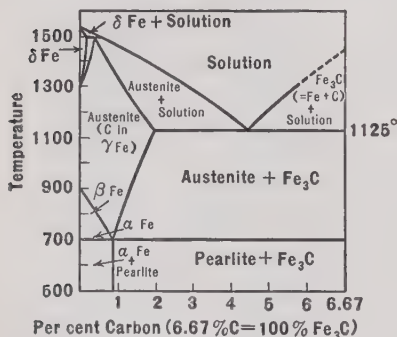


FIG. 2. The iron-carbon diagram.

of the process is not high enough to melt the pure iron and obtain a good separation from the slag. Wrought iron, while formerly of great importance, is now largely replaced by mild steel.

**6. Steel.**—Iron which contains from 0.05 to 2.0 per cent carbon and which is capable of being hardened when quenched is called steel.

The properties of steel are greatly influenced by small amounts of carbon, as may be best explained by reference to the iron-carbon diagram, Fig. 2.

If a molten solution of less than 4.2 per cent of carbon in iron is cooled, the solid which first separates is a solid solution of carbon or iron carbide in  $\gamma$ -iron, called **austenite**.



(The diagram also shows a solution in  $\delta$ -iron above  $1300^{\circ}$  but this is somewhat uncertain.) At higher concentrations of carbon, the solid phase which separates is **cementite**,  $\text{Fe}_3\text{C}$ . This is metastable in respect to the decomposition into carbon and iron, but the reaction is not rapid. The eutectic of the austenite-cementite phases lies at about  $1150^{\circ}$ .

Austenite, containing more than 0.9 per cent carbon, upon cooling yields cementite; if it contains less carbon, it yields  $\alpha$ - or  $\beta$ -iron as shown in the diagram. The eutectic temperature is  $690^{\circ}$ , and the eutectic mixture of  $\alpha$ -iron and cementite is known as **pearlite**. However, if austenite is cooled sufficiently rapidly, these transformations do not occur, and the solid solution may thus be obtained at room temperatures as a tough metal of low magnetic susceptibility.

TABLE IV

COMPOSITION AND PHYSICAL PROPERTIES OF SIMPLE CARBON STEELS

NAME	PER CENT CARBON	TENSILE STRENGTH LBS. PER SQ. IN.	ELASTIC LIMIT LBS. PER SQ. IN.
Very mild.....	0.05-0.15	45,000- 54,000	27,000-34,000
Mild.....	0.15-0.25	54,000- 68,000	34,000-40,000
Low carbon.....	0.25-0.40	68,000- 78,000	40,000-45,000
Medium carbon.....	0.40-0.60	78,000- 90,000	45,000-55,000
Higher carbon.....	0.60-0.70	90,000-100,000	54,000-64,000
Spring.....	0.70-0.80	100,000-105,000	64,000-72,000
Pearlitic.....	0.85	110,000	78,000
Hypereutectoid.....	0.85-1.5	110,000-180,000	.

Various methods of **heat treating** steel are in use. Thus if supercooled high carbon austenite is heated above  $750^{\circ}\text{C}$ . rapid equilibrium is established and some cementite separates. If the steel is held at this temperature for some time and cooled slowly the process is called **annealing**; if cooled rapidly, **quenching**. **Tempered steel** is held for some time at a temperature below the point at which rapid equilibrium is established.

The properties of the heat treated steel are thus greatly affected by the temperature and length of time of the treatment, as this determines the size of the interlacing crystals. The terms **martensite** and **sorbite** are applied to intermediate stages of the transformation of austenite into pearlite.

7. Many important special steels are made by the addition of elements other than carbon. The presence of other elements greatly modifies the temperature of the iron-carbon phase diagram. Silicon is not only highly soluble in  $\gamma$ -iron, but also catalyzes the decomposition of cementite to carbon, thus rendering the steel soft. Nickel forms a complete series of solid solutions with  $\gamma$ -iron, and since the stable form of nickel is the face-centered cubic-lattice like  $\gamma$ -iron, its presence tends to prevent the transformation of the latter into  $\alpha$ -iron. The special high speed tool-steels (Par. 19) which retain their temper at high temperatures also owe their properties, at least in part, to interference with the change of  $\gamma$ - into  $\alpha$ -iron. Reference should also be made to the metals Mn, Cr, Ni, W, V, and Mo for other special steels.

The use of **alloy cast iron** has greatly increased in recent years, the principal alloying metals being chromium, nickel, copper, and molybdenum. The following are typical compositions: automobile blocks, C, 3.3, Si, 2.2, Mn, 0.75, Cr, 0.35, Ni, 0.70, Fe, balance; brake drums, C, 3.2, Si, 2.0, Mn, 0.6, Cu, 1.0, Mo, 0.5, Fe, balance.

8. **Manufacture of Steel.**—The American production of steel is about 50 million tons annually. Various manufacturing processes are employed, depending upon the impurities present and the type of steel desired. By far the largest percentage (91.5) of the steel manufactured in the United States is made by the open-hearth process. Of the remaining, 6.8 per cent is Bessemer and 1.7 per cent electric furnace.

(a) *Open-hearth Steel.* The tremendous expansion of the steel industry in the past 50 years was rendered possible

through the development of the basic open-hearth process, whereby high-grade steel may be made from pig iron relatively high in phosphorus and sulfur.

The process consists of heating a charge of pig iron and scrap steel with sufficient iron oxide to oxidize the sulfur, phosphorus, and most of the carbon, in a furnace lined with calcined magnesite or dolomite. The carbon monoxide formed escapes as a gas, while the oxides of sulfur and phosphorus combine with the basic oxides to form a slag. The metal is contained in a shallow hearth (about 40 by 12 feet and 2 feet deep), and the heat is supplied by a gas flame directly over the surface. As mentioned above, the basic oxides also serve as a lining for the hearth. When the desired carbon content is reached, generally after about 8 hours, the heating is stopped and the melted steel is run into large ladles. Some iron low in sulfur and phosphorus is made into steel by the acid open-hearth process, which is essentially the same as the above, except that the hearth lining is silica.

(b) *Bessemer Steel*. In the Bessemer process, a blast of air is blown through molten pig iron until the impurities are oxidized. The acid process, in which the furnace is lined with silica, is applicable only to iron low in sulfur and phosphorus as these elements are not readily oxidized under these conditions. A basic lining is employed in certain European districts, which permits the removal of the phosphorus in the basic slag; however, the iron must be low in sulfur.

The Bessemer converter is a large egg-shaped vessel mounted on trunnions so as to turn about its shorter axis. The molten metal is poured in through the necklike opening in the top, while the converter is in a horizontal position. The air-blast, which enters through perforations in the bottom, is then turned on, and the converter raised to an upright position. The heats of combustion of the carbon and silicon keep the metal molten in spite of the higher melting

point of the pure iron. The "blow" is finished in about ten minutes, and the converter is turned on its side so that a calculated quantity of carbon, manganese, or other metals may be added.

(c) *Crucible and Electrothermal Steel.* The finest grades of tool-steel have long been made by heating wrought iron with pure carbon in small crucibles, and the product is known as crucible steel. Much of the high-grade steel is made in small electrically heated furnaces. The method is similar to the open-hearth process, except that the mode of heating permits more careful control. Most of the electric furnace product is alloy steel.

(d) *Case-hardened Steel.* In the manufacture of armor plate, and many auto and other machine parts, it is often desirable to harden the surface and at the same time keep the toughness of the body of the metal. This is accomplished by heating the article, packed in carbon or in cyanide, until the desired amount of carbon is absorbed into the surface. Another form of surface hardening called **nitriding** consists in heating an alloy steel (usually containing Al, Cr, or Mo) in an atmosphere of ammonia. Nitrides of the alloying metals are thus formed on the surface.

**9. Reactions of Iron.**—Iron is a good reducing agent at ordinary temperature, and a very powerful reducing agent at high temperature, combining readily with all of the negative elements (Table V).

Iron and oxygen do not react in the cold, but when heated they form ferroferric oxide,  $\text{Fe}_3\text{O}_4$ ; and at higher temperatures ferric oxide,  $\text{Fe}_2\text{O}_3$ .

The equilibria between iron, iron oxides, and steam are of considerable importance; and the ratios of  $\text{H}_2\text{O}/\text{H}_2$  for the systems,  $\text{Fe} : \text{FeO}$  and  $\text{FeO} : \text{Fe}_3\text{O}_4$ , and given in Table V. The solid phases in these systems appear to be solid solutions.

At lower temperatures the reaction is entirely  $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$ , as ferrous oxide is unstable in

TABLE V  
CONSTANTS FOR THE IRON AND STEAM EQUILIBRIA

		700°	800°	900°	1000° C.
$\text{FeO} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O}$	$\text{H}_2\text{O}/\text{H}_2$	0.584	0.706	0.822	0.937
$\text{Fe}_3\text{O}_4 + \text{H}_2 = 3\text{FeO} + \text{H}_2\text{O}$	$\text{H}_2\text{O}/\text{H}_2$	1.45	2.98	5.50	9.12

respect to iron and  $\text{Fe}_3\text{O}_4$  below 570°; and at 400°, the ratio,  $\text{H}_2\text{O}/\text{H}_2$ , in this equilibrium is about 0.2.

The equilibria between iron, iron oxides, and the oxides of carbon have been discussed in connection with the blast furnace, Par. 4.

Iron dissolves in dilute acids with the evolution of hydrogen and the formation of ferrous salts. Strong oxidizing agents yield ferric compounds, but very powerful oxidizing agents, such as concentrated nitric acid or dichromate, render the metal passive; and in this condition it is not dissolved by hydrogen ion nor will it reduce cupric solutions. Passivity is destroyed by scratching the surface, by the action of reducing agents, or by placing the metal in a powerful magnetic field. The phenomenon appears to be due to the formation of a surface film of oxide.

The **rusting** of iron involves two steps: (1) the oxidation to ferrous ion by acid, usually carbonic, i.e.  $\text{Fe} + 2\text{H}_2\text{CO}_3 = \text{Fe}^{++} + 2\text{HCO}_3^- + \text{H}_2$  and (2) the formation of ferric oxide (iron rust) by the atmospheric oxygen:  $4\text{Fe}^{++} + 8\text{HCO}_3^- + \text{O}_2 + 7\text{H}_2\text{O} = 2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + 8\text{H}_2\text{CO}_3$ .

The first step does not take place readily with pure iron, due to the over-voltage effect of hydrogen on the metal. Rusting is, therefore, favored by the presence of impurities which present surfaces for the escape of the gas. Pure water is about equal to ferrous ion as an oxidizing agent (Append. II), so there is not much driving power to the solution of the metal in pure water; the reaction is, of course, favored by increasing the concentration of hydrogen ion.



TABLE VI  
REACTIONS OF IRON

$3\text{Fe} + 2\text{O}_2 = \text{Fe}_3\text{O}_4$	Readily at $500^\circ$ , $\text{Fe}_2\text{O}_3$ at higher temp.
$\text{Fe} + \text{S} = \text{FeS}$	Heated
$2\text{Fe} + 3\text{X}_2 = 2\text{FeX}_3$	Halogens except $\text{I}_2$ which gives $\text{FeI}_2$
$2\text{Fe} + 2\text{H}^+ = \text{Fe}^{++} + \text{H}_2$	Reaction potential + 0.44 volt
$3\text{Fe} + \text{C} = \text{Fe}_3\text{C}$	Above $1,200^\circ$
$\text{Fe} + \text{Si} = \text{FeSi}$	Also $\text{Fe}_2\text{Si}$
$3\text{Fe} + \text{P} = \text{Fe}_3\text{P}$	
$3\text{Fe} + 4\text{H}_2\text{O}_{(\text{steam})} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$	See Table V
$\text{Fe} + 5\text{CO} = \text{Fe}(\text{CO})_5$	See Par. 15
$\text{Fe} + \text{CO}_2 = \text{FeO} + \text{CO}$	See Table III
$4\text{Fe} + 2\text{NH}_3 = 2\text{Fe}_2\text{N} + 3\text{H}_2$	Fe does not react directly with $\text{N}_2$

### COMPOUNDS OF IRON

**10. Oxidation States.**—Iron forms two important series of salts: ferrous, with an oxidation state of + 2, and ferric, with an oxidation state of + 3. In addition, salts are known of ferrate ion,  $\text{FeO}_4^{--}$ , in which iron has the + 6 oxidation state and there is some evidence for perferriate,  $\text{FeO}_3^{--}$ .

Oxidation-reduction potentials relating to the oxidation states are given below:

	VOLTS
$\text{Fe} = \text{Fe}^{++} + 2e^-$ .....	+ 0.44
$\text{Fe} + 2\text{OH}^- = \text{Fe}(\text{OH})_2 + 2e^-$ .....	+ 0.88
$\text{Fe}^{++} = \text{Fe}^{+++} + e^-$ .....	- 0.77
$\text{Fe}(\text{OH})_2 + \text{OH}^- = \text{Fe}(\text{OH})_3 + e^-$ .....	+ 0.56
$\text{Fe}(\text{CN})_6^{--} = \text{Fe}(\text{CN})_6^{---} + e^-$ .....	(- 0.49)
$\text{Fe}^{+++} + 4\text{H}_2\text{O} = \text{FeO}_4^{--} + 8\text{H}^+ + 3e^-$ .....	< - 1.9
$\text{Fe}(\text{OH})_3 + 5\text{OH}^- = \text{FeO}_4^{--} + 4\text{H}_2\text{O} + 3e^-$ .....	< - 0.9

It follows from these values that the reaction,  $\text{Fe} + 2\text{Fe}^{+++} = 3\text{Fe}^{++}$ , is practically quantitative. Also ferrous iron is readily oxidized to ferric in alkaline solution, but much less readily in acid; in fact, acid ferrous solutions are oxidized to ferric only very slowly by the air, as the reaction potential is above that of oxygen to hydrogen peroxide (Append. II), which is the first step of the oxygen reaction. The ferrates are such powerful oxidizing agents that they are difficult to prepare, and very unstable.

**11. Ferrous Compounds.**—Ferrous compounds resemble manganous in their solubilities. The **hydroxide**,  $\text{Fe}(\text{OH})_2$ ,



is precipitated from ferrous solutions by alkalies, but it is only moderately insoluble in water and its solubility is greatly increased in ammonium salts. The pure hydroxide is white, but in the air it quickly turns green, and then reddish-brown through oxidation to ferric hydroxide. The **oxide**,  $\text{FeO}$ , may be prepared by heating the oxalate, but the product contains some iron and ferric oxide. It burns when heated in air. Ferrous ion has a pale green color.

**Ferrous sulfide** forms through the direct union of the elements. It forms as a black precipitate when soluble sulfides are added to neutral or basic ferrous solutions, but is readily soluble in acids. The naturally occurring sulfide generally contains an excess of sulfur in solid solution. Ferrous sulfide combines with sulfur to form the **disulfide**,  $\text{FeS}_2$ , known as **iron pyrites** or "fools' gold." It occurs in nature as brass-colored cubic crystals. It is not dissolved by dilute acids, but is slowly decomposed by concentrated hydrochloric acid,  $\text{FeS}_2 + 2\text{HCl} = \text{FeCl}_2 + \text{H}_2\text{S} + \text{S}$ , and rapidly by nitric acid with the oxidation of the sulfur. An orthorhombic modification called **marcasite** also occurs. Pyrite is an important source of sulfur for the manufacture of sulfuric acid.

**Ferrous sulfate**,  $\text{FeSO}_4$ , is the most important ferrous salt. It is prepared commercially by the oxidation of moist pyrites:  $2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} = 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$ . The hydrate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , which crystallizes upon evaporation of the water solution, is known as green vitriol or copperas. It is used as a disinfectant, in the manufacture of dyes, and in the preparation of ink.

The common black or blue **inks** contain the ferrous salt of gallotannic acid. This is not colored, but upon exposure to the air the black ferric salt is precipitated. A black or blue dye gives the initial color of the ink.

**Ferrous ammonium sulfate**,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , may be crystallized from equimolar solutions of the two sulfates. This salt is very stable toward oxidation by the air, and is

employed as a primary standard in quantitative analysis (cf. XVIII—12).

**Ferrous carbonate**,  $\text{FeCO}_3$ , is readily precipitated from ferrous solutions by soluble carbonates. It occurs in nature as the mineral, siderite.

**Ferrous halides** are readily soluble in water. They may be prepared by various methods, e.g. by dissolving the metal in the halogen acid, or by the action of the halogen upon excess of the metal.

**Ferrous oxalate**,  $\text{FeC}_2\text{O}_4$ , forms as a yellow precipitate upon the addition of oxalate to a ferrous solution. With excess reagent, it dissolves with the formation of a yellowish red solution containing the complex ion,  $\text{Fe}(\text{C}_2\text{O}_4)_2^{--}$ .

Aqueous solutions of ferrous ion absorb nitric oxide with the formation of the **ferronitroso complex ion**,  $\text{FeNO}^{++}$ . This is the basis of the "ring test" for nitrates (cf. XI—39).

The complex **ferrous cyanides** are discussed in Paragraph 13.

**12. Ferric Compounds.**—**Ferric oxide**,  $\text{Fe}_2\text{O}_3$ , and its hydrate,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , are the most important ores of iron. In the various complex minerals containing this oxide, it generally behaves as an acid oxide, its salts being known as **ferrites**. One of the most common of these compounds is **ferrous ferrite** or **magnetite**,  $\text{Fe}_3\text{O}_4$ , i.e.  $\text{Fe}(\text{FeO}_2)_2$ . As its common name indicates, it is highly magnetic, and large specimens are known as "lode stones." Ferrites may be prepared by fusing ferric oxide with basic oxides, e.g.  $\text{NaFeO}_2$ ,  $\text{Ca}(\text{FeO}_2)_2$ , and **ferrous acid**,  $\text{HFeO}_2$ , is obtained by the action of water upon sodium ferrite. The oxide exists in many modifications.  $\alpha\text{-Fe}_2\text{O}_3$ , hematite, varies in color from yellow to dark red depending upon the state of subdivision. The ferromagnetic, or  $\gamma\text{-Fe}_2\text{O}_3$  also is yellow to red.

Around  $3000^\circ$  ferric oxide loses oxygen to form magnetite, but at lower temperatures, about  $1300^\circ$ , the reaction is slowly reversed:  $4\text{Fe}_3\text{O}_4 + \text{O}_2 = 6\text{Fe}_2\text{O}_3$ .

Finely divided ferric oxide under the names "**rouge**" and "**Venetian red**," is used as an abrasive and as a pigment.

Four forms of precipitated ferric oxide, so-called **ferric hydroxide**, are known. The addition of alkali to ferric solutions precipitates the brown gel which is hydrous  $\alpha\text{-Fe}_2\text{O}_3$ . The slow hydrolysis of most ferric salts yields  $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$  which dehydrates to  $\alpha\text{-Fe}_2\text{O}_3$ . The hydrolysis of ferric chloride forms  $\beta\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ . This also gives  $\alpha\text{-Fe}_2\text{O}_3$  upon dehydration. The oxidation of ferrous compounds and solutions with certain oxidizing agents forms  $\gamma\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$  which gives  $\gamma\text{-Fe}_2\text{O}_3$  on dehydration. Ferric oxide sols are remarkably stable. They are ordinarily positively charged and may be coagulated by negative ions, but if the negative ion is strongly adsorbed, a reversal of the sign of the charge may occur with the formation of a negative sol.

Ferric oxide is a weak base, and in water solution shows but slightly the acid properties exhibited by the oxide in its mineral compounds, in that it is not soluble in excess of dilute alkali, and only slightly in concentrated alkali.

Due to the weak basic properties of ferric hydroxide, ferric salts are highly hydrolyzed, and their characteristic yellow brown color in solution appears to be due to the colloidal hydroxide or to basic ions. When this is repressed by acid, the yellow color becomes lighter.

**Ferric halides**, except the iodide, may be prepared by the action of the halogen upon the metal, or by dissolving the hydroxide in acid. Iodide ion is oxidized by ferric ion:  $2\text{Fe}^{+++} + 2\text{I}^- = 2\text{Fe}^{++} + \text{I}_2$ , but the reaction is not complete unless the equilibrium is displaced by the removal of the  $\text{I}_2$ . The halides are very soluble, forming many hydrates. With excess of halide ion, they form **complex halides**; and many of the complex salts are known, e.g.  $\text{K}_3\text{FeF}_6$  and  $(\text{NH}_4)_3\text{FeCl}_6$ .

Magnetic data indicate that these complex ions are ionic in character and not covalent as, for example, are the com-

plex cyanides. The fluoride is quite stable and in solution does not oxidize iodide.

Hydrogen sulfide in acid solution reduces ferric salts to ferrous with the precipitation of sulfur, but if ammonium sulfide is used, **ferric sulfide**,  $\text{Fe}_2\text{S}_3$ , is precipitated. The pure compound is unstable, but ferric sulfide complexes with other metallic sulfides occur in nature.

**Ferric sulfate**,  $\text{Fe}_2(\text{SO}_4)_3$ , and **ferric nitrate**,  $\text{Fe}(\text{NO}_3)_3$ , are both soluble, but tend to form basic salts by hydrolysis. The former, like most sulfates of + 3 ions, forms **alums**, e.g.  $\text{KFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

**Ferric phosphate**,  $\text{FePO}_4$ , is a common constituent of phosphate rock. It is very slightly soluble, and may be precipitated from an acetic acid solution of ferric ion. It is, however, soluble in strong acids.

Ferric ion, like the ferrous, also forms a **complex oxalate ion**,  $\text{Fe}(\text{C}_2\text{O}_4)_3^{--}$ , which accounts for the use of oxalic acid in removing ink and iron rust spots from fabrics. The soluble red **thiocyanate**  $\text{Fe}(\text{SCN})_3$  forms the complex ion,  $\text{Fe}(\text{SCN})_6^{-3}$ , with excess of thiocyanate.

**13. Complex Iron Cyanides.**—Both ferrous and ferric ion form complex ions with excess cyanide, the former yielding **ferrocyanide**,  $\text{Fe}(\text{CN})_6^{-4}$ , and the latter **ferricyanide**,  $\text{Fe}(\text{CN})_6^{-3}$ . These complex ions are so stable that their solutions show virtually none of the properties of the iron or cyanide ions. The structure of these ions is octohedral, which is the general structure of covalent complexes which involve two *d*, one *s*, and three *p* orbitals of the central atom.

**Sodium and potassium ferrocyanide**,  $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ , and  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ , are usually prepared as by-products from the distillation of coal. A considerable portion of the nitrogen in coal is liberated as hydrogen cyanide,  $\text{HCN}$ . This is absorbed in iron oxide purifiers as iron cyanide, which is then treated with lime to form calcium ferrocyanide; this, in turn, is converted into the alkali ferrocyanide. Formerly, the ferrocyanides were prepared by fusing nitrog-

enous material with potash and iron turnings. The potassium compound is commonly called "**yellow prussiate of potash**." The hydrates decompose at about  $100^{\circ}$ , yielding colorless powders which ignite when heated in air. With concentrated sulfuric acid the cyanide ion is slowly hydrolyzed, forming ammonium ion and carbon monoxide:  $\text{K}_4\text{Fe}(\text{CN})_6 + 6\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} = 2\text{K}_2\text{SO}_4 + \text{FeSO}_4 + 3(\text{NH}_4)_2\text{SO}_4 + 6\text{CO}$ . When heated with metallic sodium, the iron is reduced and a mixture of metallic iron and alkali cyanide formed. With hydrochloric acid, the weak **hydroferrocyanic acid**,  $\text{H}_4\text{Fe}(\text{CN})_6$ , is formed. This acid may be extracted from concentrated water solution by ether, from which it crystallizes as a colorless compound, stable in dry air, but readily oxidized in moist air.

The ferrocyanide-ferricyanide couple possesses moderately strong oxidizing power. The value of the potential given in Par. 10 is for equal concentration of the two ions and is not corrected for the activities, the  $E^{\circ}$  value is around  $-0.36$ . Ferrocyanides are readily converted into ferricyanides by the action of chlorine in solution. The commercial preparation of **potassium ferricyanide** or "**red prussiate of potash**,"  $\text{K}_3\text{Fe}(\text{CN})_6$ , depends upon this oxidation. The ferricyanide ion is not as stable as the ferrous complex, and decomposes slowly in the sunlight.

Alkali ferrocyanides form with ferric ion, first a soluble blue compound,  $\text{KFe}_2(\text{CN})_6$ , called potassium berlineate or soluble Prussian blue, and then a very slightly soluble precipitate of **Prussian blue**,  $\text{Fe}_7\text{C}_{18}\text{N}_{18} \cdot 10\text{H}_2\text{O}$ , (*vide infra*), which is an important blue pigment. With ferrous ion, potassium ferrocyanide forms a white precipitate of potassium ferrous-ferrocyanide,  $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ . A number of the ferrocyanides are important in analytical chemistry, especially the compounds with zinc and uranium,  $\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$  and  $\text{K}_2\text{UO}_2[\text{Fe}(\text{CN})_6]$ .

Ferricyanide yields with ferric ion a deep brown solution, probably of undissociated ferric ferricyanide. With ferrous



ion a precipitate, Turnbull's blue, is formed. From X-ray analysis the structure of solid ferric ferricyanide has been determined as a cubic sodium chloride lattice. Each ferricyanide ion is thus surrounded by six ferric ions and the cyanide ion serves as a bond between the iron ions,  $\text{FeCNFe}$ . The structure of potassium berlineate is similar except that alternate small cubes contain a  $\text{K}^+$  in the center. The relation of the iron and cyanide is also the same in the potassium ferrous-ferrocyanide,  $\text{K}_2\text{FeFe}(\text{CN})_6$ , but in this case each small cube is occupied by a  $\text{K}^+$ . Prussian blue appears to be ferric berlineate  $\text{Fe}[\text{FeFe}(\text{CN})_6]_3$  and the Turnbull's blue ferrous berlineate,  $\text{Fe}[\text{FeFe}(\text{CN})_6]_2$ . The linkage between the berlineate ions in the solid is probably of the same type as that found for  $\text{FeFe}(\text{CN})_6$ . A number of copper ferrocyanides are known which are probably derivatives of similar supercomplexes, e.g.,  $\text{Cu}[\text{CuFe}(\text{CN})_6]$ , and  $\text{K}_2[\text{CuFe}(\text{CN})_6]$ . Zinc, however, appears to be unable to coordinate with six cyanides and the supercomplex structure is more complicated, e.g.  $[\text{Zn}_3[\text{Fe}(\text{CN})_6]_2]^{-2}$ .

**Blue print paper** is made by treating paper with a solution of ammonium ferricyanide and ferric citrate in the dark. When exposed to light, reduction of the iron by the citrate takes place with the formation of Prussian blue. The print is fixed by washing out the unchanged mixture with water.

One of the cyanide groups, in either the ferro- or ferricyanide, may be replaced by other groups; e.g.  $\text{NO}$ ,  $\text{CO}$ ,  $\text{SO}_3^{--}$ ,  $\text{NO}_2^-$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{AsO}_2^-$ , forming **complex pentacyanides**. **Sodium ferri-nitrosopentacyanide**,  $\text{Na}_2\text{FeNO}(\text{CN})_5 \cdot 2\text{H}_2\text{O}$ , gives an intense blue color with sulfide in alkaline solutions, thus constituting a delicate test for the latter substance.

**14. Perferrites and Ferrates.**—**Barium and strontium perferrites**,  $\text{BaFeO}_3$ , and  $\text{SrFeO}_3$ , have been prepared by heating mixtures of the hydroxide with ferric hydroxide in a current of oxygen. The compounds are decomposed by water, and there is but slight evidence for the formation of



the dioxide of iron. The ferryl ion,  $\text{FeO}^{++}$ , may possibly exist at low concentrations under some conditions.

Powerful oxidizing agents in fused alkali or in very concentrated alkaline solution oxidize ferric hydroxide to **ferrate**. **Barium ferrate**,  $\text{BaFeO}_4$ , analogous to the sulfate, is but slightly soluble and is the most stable of the ferrates. It is not decomposed by water or cold dilute sulfuric acid; but with cold hydrochloric acid, chlorine and oxygen are evolved, though the solution first assumes the red color characteristic of  $\text{FeO}_4^{--}$ .

**15. Iron Carbonyls.**—Finely divided iron reacts slowly with carbon monoxide to form the **pentacarbonyl**,  $\text{Fe}(\text{CO})_5$ , which may be distilled off by heating to  $120^\circ$ . This substance freezes at  $-21^\circ$ , boils at  $102^\circ$ , and decomposes when heated above  $200^\circ$ . In the sunlight it decomposes:  $2\text{Fe}(\text{CO})_5 = \text{Fe}_2(\text{CO})_9 + \text{CO}$ . This latter compound decomposes upon heating to form  $\text{Fe}_3(\text{CO})_{12}$ . The pentacarbonyl dissolves in alkalis:  $\text{Fe}(\text{CO})_5 + 4\text{OH}^- = \text{Fe}(\text{CO})_4^{--} + \text{CO}_3^{--} + 2\text{H}_2\text{O}$ . Upon acidifying in the cold the **carbonyl hydride**,  $\text{Fe}(\text{CO})_4\text{H}_2$ , is liberated. This carbonyl hydride has acid properties and forms many salts. When oxidized with hydrogen peroxide it forms  $\text{Fe}_3(\text{CO})_{12}$ , and when warmed it decomposes:  $2\text{Fe}(\text{CO})_4\text{H}_2 = \text{Fe}(\text{CO})_5 + \text{Fe}(\text{CO})_3$  (polymerized)  $+ 2\text{H}_2$ . The mercuric salt is prepared by oxidizing the pentacarbonyl with mercuric chloride:  $\text{Fe}(\text{CO})_5 + \text{H}_2\text{O} + \text{HgCl}_2 = \text{Fe}(\text{CO})_4\text{Hg} + 2\text{HCl} + \text{CO}_2$ . The structure of

$\text{Fe}_2(\text{CO})_9$  appears to be  $(\text{CO})_3\text{Fe} \begin{array}{c} \diagup \text{OC} \diagdown \\ \text{CO} \end{array} \text{Fe}(\text{CO})_3$ . It may

be noted that in all of these compounds the iron atom has the same number of electrons (if the two shared with each CO is included) as has the next inert gas krypton. The same is true of the nitrosyl carbonyl  $\text{Fe}(\text{CO})_2(\text{NO})_2$  if one assumes that the odd electron on the nitric oxide has transferred to the iron.

**16. Analytical.**—The formation of Prussian blue, through the reaction of ferrocyanide with ferric ion, and ferricyanide with ferrous ion, serve to identify iron in both of the common valence states. Ferric iron may be distinguished also by the deep red color of **ferrisulfocyanide**,  $\text{Fe}(\text{SCN})_3$ , and a bright red compound with pyrocatechol.

In the scheme for the systematic separation of the elements, iron salts are precipitated by ammonium sulfide and hydroxide as ferrous sulfide. The general method of separation from the other members of this analytical group is indicated in Appendix VI. In case phosphate is present, the analytical procedure requires some modification, because ammonium hydroxide will precipitate ferric phosphate from ferric solutions.

The so-called **basic acetate separation**, which is often used in the iron group, is carried out by the addition of ammonium acetate to a slightly acid solution. Upon heating, hydrolysis occurs; and the precipitate may contain Fe, Ga, Cr, V, W, Al, In, Zr, Ti, as hydroxides, basic acetates, phosphates, or vanadates, and the rare earths (if phosphate is present). The method serves to separate these elements from Mn, Zn, Co, Ni, U, alkaline earths, and rare earths (if phosphate is not present), although traces of Zn, Co, Ni, Be, and U may be present in the precipitate.

In gravimetric analysis, iron is usually precipitated as ferric hydroxide by ammonium hydroxide and weighed as ferric oxide. The reagent, "**cupferron**,"  $\text{C}_6\text{H}_5\text{N}\cdot\text{NO}\cdot\text{ONH}_4$ , is sometimes used to precipitate iron as the ferric salt. This method has the advantage of precipitating iron (and also Cu, Ti, and Zr) from highly acid solutions, and thus effecting a separation from Al, Cr, Mn, Ni, and Co. When treated with ammonium hydroxide, the precipitate is changed to ferric hydroxide.

Iron is determined in volumetric analysis usually by one of the two reactions:  $5\text{Fe}^{++} + \text{MnO}_4^- + 8\text{H}^+ = \text{Mn}^{++} + 5\text{Fe}^{+++} + 4\text{H}_2\text{O}$ , and  $6\text{Fe}^{++} + \text{Cr}_2\text{O}_7^{--} + 14\text{H}^+$

$= 6\text{Fe}^{+++} + 2\text{Cr}^{+++} + 7\text{H}_2\text{O}$ . In the dichromate method the end-point is determined by removing a drop of the solution and testing with ferricyanide, or by the addition of an oxidation indicator, e.g., diphenylamine which gives a blue color upon oxidation. In the permanganate method the color of the reagent serves as an end-point indicator. The dichromate method is readily applicable in the presence of chloride, but permanganate tends to evolve chlorine under these conditions, unless an excess of manganous ion is added (cf. XVIII—12).

In the preparation of the ferrous solution before titration, ferric iron may be reduced in various ways, but the most generally employed methods are: (1) reduction by passing the solution through a tube containing zinc amalgam (Jones reductor), (2) reduction with stannous chloride followed by removal of excess stannous ion by mercuric chloride.

Ferric salts in solution may also be titrated directly with titanous chloride, using thiocyanate as an indicator:  $\text{Fe}^{+++} + \text{Ti}^{+++} = \text{Fe}^{++} + \text{Ti}^{++++}$ .

## COBALT AND NICKEL

**17. Occurrence.**—Nickel ranks next to iron in abundance in meteoric material, and it seems probable that this order also exists in the central core of the earth. However, in the igneous rocks on the earth's crust, the estimated percentage of nickel is 0.020 and cobalt  $1 \times 10^{-5}$ .

The commonest cobalt minerals are: smaltite,  $\text{CoAs}_2$ ; cobaltite,  $\text{CoAsS}$ ; erythrite,  $\text{Co}_3(\text{AsO}_4) \cdot 8\text{H}_2\text{O}$ ; and linnaeite,  $\text{Co}_3\text{S}_4$ . These ores are generally associated with iron, and often nickel, copper, and silver. The principal source of cobalt is the rich silver-cobalt-nickel veins in Ontario, Canada.

The two most important nickel ores are: pentlandite,  $\text{NiS} \cdot 2\text{FeS}$ , and garnierite,  $[\text{Ni}, \text{Mg}]\text{SiO}_3 \cdot n\text{H}_2\text{O}$ . Extensive deposits of the former mixed with iron and copper sulfide

are found in Ontario, Canada, and of the latter in New Caledonia. Nickel also occurs in other complex sulfides, silicates, arsenides, arsenates, tellurides, oxides, and sulfates. Copper ores usually contain small amounts of nickel, which are removed in the electrolytic refining process.

**18. Metallurgy.**—The cobalt-silver arsenide ore of Ontario is smelted with a suitable flux in a small blast furnace, yielding crude silver bullion, and a speiss of the arsenides of cobalt, nickel, iron, copper, and some silver. This speiss is subjected to successive roasting processes; with silica to remove iron; with sodium nitrate and carbonate to form sodium arsenate; and with salt to form chlorides of cobalt, nickel, copper, and silver. The soluble chloride is extracted with water; the copper precipitated as the metal by reduction, and the cobalt and nickel precipitated as hydroxides.

The separation of cobalt and nickel is effected by the Mond process (see below), or by the formation of potassium cobaltinitrite (Par. 24), or chloropentammine cobaltichloride (Par. 24). The metal is made by reducing the oxide with carbon.

The metallurgy of nickel ores is somewhat similar. The product of the blast furnace smelting is a matte of iron, copper, and nickel sulfides. This matte is freed from much of the iron by oxidizing in a Bessemer converter with a silicate slag.

In the Orford process, the Bessemer matte is fused with carbon and sodium sulfate, which effects a separation of rather pure nickel sulfide in the bottom layer. This sulfide is roasted to the oxide, and reduced by carbon to the metal.

In the Mond process, the matte is roasted to the oxide, reduced to the metal by water gas at  $300^{\circ}$ , and the nickel removed by volatilization as the carbonyl,  $\text{Ni}(\text{CO})_4$ , in a stream of carbon monoxide at a temperature of  $50^{\circ}$  to  $100^{\circ}$ . The carbonyl is then decomposed into the metal and carbon monoxide by heating.

Electrolytic refinement of nickel is also employed. The

impure metal is made the anode in a cell using nickel sulfate electrolyte. The pure metal is precipitated on an aluminum cathode. The platinum metals precipitate in the anode mud and the base metals remain in the electrolyte.

**19. The Metals.**—The important atomic and physical constants of the metals are given in Table VII. Unlike iron, cobalt and nickel do not have at low temperatures a body centered cubic type of crystal lattice, but are face centered. They do, however, process magnetic transitions similar to iron; and the non-magnetic forms are isomorphous with the face centered, or  $\gamma$ -iron. The metals are silver-grey in color, malleable, and ductile.

TABLE VII  
ATOMIC AND PHYSICAL PROPERTIES OF COBALT AND NICKEL

	Co	Ni
Atomic weight.....	58.94	58.69
Atomic number.....	27	28
Isotopes.....	57, 59	58, 60, 61, 62, 64
Density.....	8.9	8.9
Melting point, ° C.....	1490	1452
Boiling point, ° C.....	2900	2730
Radius of $M^{++}$ in solids, cm. $\times 10^8$ .....	0.72	0.69
Electrical resistivity, ohm-cm.....	$9.7 \times 10^{-6}$	$6.9 \times 10^{-6}$
Tensile strength, lb. per sq. in.....	35000 (cast)	150000 (drawn)
Transition temperature, magnetic to non-magnetic form, ° C.....	1150	360

Cobalt does not at present have extensive industrial applications. Its most important use is as a constituent of the group of alloys known as **stellite**, which contain cobalt and one or more of the metals chromium, tungsten, molybdenum, iron, and nickel. Representative composition of two such alloys are: (1) Co 60, Cr 15, W 20, Mo 5, and (2) Co 30, Fe 52, W 14, Cr 4. These alloys are used as cutting tools in high-speed lathes, as they do not lose their edge with heating; and also as surgical instruments, since they may be sterilized in a flame without injury to the edge or

polish. Cobalt is also used in making cobalt steel for permanent magnets, the alloy alnico, containing aluminum, nickel and cobalt, is capable of lifting 60 times its own weight when magnetized. Cobalt-thorium catalysts are employed in the Fischer-Tropsch production of gasoline from coal.

The electrolytic nickel plating industry is one of the largest consumers of nickel. The plated coat is hard, susceptible of high polishing, and is resistant to tarnishing. The electrolyte generally employed is nickel ammonium sulfate.

Finely divided or "active" nickel, prepared by reducing the oxide below 300°, is employed as a catalyst in a number of hydrogenation reactions; the most important commercially being the hardening of fats and oils by their combination with hydrogen, and the conversion of carbon monoxide and steam into carbon dioxide and hydrogen.

TABLE VIII  
NICKEL ALLOYS

NAME	PERCENTAGE COMPOSITION	PROPERTIES AND USES
Low nickel steel.....	Ni 0.5–2.0, C 0.15, Fe about 96 (often 0.5–1.5 Cu)	Automobiles, railway cars, armor plate
Invar.....	Ni 35, Mn 0.5, C 0.5, Fe 64	Low coef. of expansion
Platenite.....	Ni 46, C 0.15, Fe 54	Glass to metal seals
Monel.....	Ni 60, Cu 36, Fe 3.5, Al 0.5	Low heat conductivity, casts, non-corroding
Nickel coins.....	Ni 25, Cu 75	Coins
Constantan.....	Ni 40, Cu 60	Thermoelements
Manganin.....	Ni 4, Mn 12, Cu 84	Electrical resistance wire
German silver.....	Ni 20, Cu 55, Zn 25	Jewelry
Nichrome.....	Ni 60, Cr 15, Fe 25	Electrical resistance; crucibles
Illium.....	Ni 62, Cu 7, Cr 22, Mo 8, Fe 1	Acid resisting

Nickel forms an unusually large number of alloys of technical importance (Table VIII). Approximately half of the 40–50 million pounds of the metal consumed annually



in the United States goes into nickel steel and 25 per cent into other alloys.

**20. Reactions of the Metals.**—The difficulty of oxidation increases gradually in going from iron to cobalt and nickel (see Par. 21 and Par. 27 for potential values), but in general the reactions of the three metals are similar. Like iron, they are rendered passive by very powerful oxidizing agents. The principal reactions are summarized in Table IX.

TABLE IX  
REACTIONS OF COBALT AND NICKEL

$3\text{Co} + 2\text{O}_2 = \text{Co}_3\text{O}_4$	
$2\text{Ni} + \text{O}_2 = 2\text{NiO}$	
$\text{M} + 2\text{H}^+ = \text{M}^{++} + \text{H}_2$	Slow at 25°. Cf. Pars. 21 and 27
$\text{M} + \text{H}_2\text{O} = \text{MO} + \text{H}_2$	Slow at red heat
$3\text{M} + 2\text{NO}_3^- + 8\text{H}^+ = 3\text{M}^{++} + 2\text{NO} + 4\text{H}_2\text{O}$	Passive with concentrated acid
$\text{M} + \text{X}_2 = \text{MX}_2$	With halogens. Co also forms $\text{CoF}_3$
$4\text{M} + 2\text{NH}_3 = \text{M}_4\text{N}_2 + 3\text{H}_2$	400 to 600°
$3\text{M} + \text{C} = \text{M}_3\text{C}$	Carbides stable only at temperatures of the molten metals
$\text{M} + 4\text{CO} = \text{M}(\text{CO})_4$	Below 100° but with Co only under pressure
$2\text{M} + \text{Si} = \text{M}_2\text{Si}$	Co also forms $\text{CoSi}$ , $\text{CoSi}_2$ , and $\text{CoSi}_3$ , and Ni forms $\text{NiSi}$ and $\text{Ni}_3\text{Si}_2$
$\text{M} + \text{S} = \text{MS}$	

### COMPOUNDS OF COBALT

**21. Oxidation States.**—Cobalt, like iron, forms cobaltous,  $\text{Co}^{++}$ , and cobaltic,  $\text{Co}^{+++}$ , ions and compounds, and a few cobaltites, derivatives of the dioxide,  $\text{CoO}_2$ , which, unlike the corresponding iron oxide, has been prepared. The cobaltic ion is a very powerful oxidizing agent, and for this reason its compounds are not very stable, except those complexes which give a very small concentration of the metal ion. Potential values are summarized below:

	VOLTS 25°
$\text{Co} = \text{Co}^{++} + 2e^-$ .....	+ 0.277
$\text{Co}^{++} = \text{Co}^{+++} + 2e^-$ .....	- 1.84
$\text{Co} + 2\text{OH}^- = \text{Co}(\text{OH})_2 + 2e^-$ .....	+ 0.42
$\text{Co}(\text{OH})_2 + \text{OH}^- = \text{Co}(\text{OH})_3 + e^-$ .....	- 0.2
$\text{Co}(\text{OH})_3 + \text{OH}^- = \text{CoO}_2 + 2\text{H}_2\text{O} + e^-$ .....	- 1.2
$\text{Co}(\text{CN})_6^{-4} = \text{Co}(\text{CN})_6^{-3} + e^-$ .....	+ 0.8

**22. Cobaltous Compounds.**—**Cobaltous oxide**,  $\text{CoO}$ , may be prepared by the reduction of the higher oxides with hydrogen. When heated in air, it forms the cobaltous cobaltic oxide,  $\text{Co}_3\text{O}_4$ . The rose-colored hydroxide  $\text{Co}(\text{OH})_2$  is precipitated when alkali hydroxides are added to cobaltous solutions but darkens in the air through oxidation to cobaltic hydroxide. With concentrated ammonia the hydroxide dissolves to form  $\text{Co}(\text{NH}_3)_6^{++}$ , with excess of  $\text{Co}^{++}$  a green or blue modification of  $\text{Co}(\text{OH})_2$  is precipitated by hydroxide.

**Cobaltous halides** are readily formed by dissolving the hydroxide in the halogen acid. They are soluble and form a number of hydrates. The **chloride** is sometimes used as a "sympathetic ink," by writing with a solution of the pale pink hexahydrate; the characters are invisible but appear upon warming the paper, due to the formation of the blue anhydrous salt. The color of the ion  $\text{Co}(\text{H}_2\text{O})_6^{++}$  is pink and that of the complex chloride  $\text{CoCl}_4^{--}$ , blue. It has been suggested that upon dehydration, the hexahydrate,  $\text{Co}(\text{H}_2\text{O})_6\text{Cl}_2$  forms the complex salt  $\text{Co}(\text{CoCl}_4)$ .

The **sulfate** and **nitrate** are soluble and highly hydrated, and the latter readily decomposes to the sesquioxide upon heating.

**Cobaltous sulfide** is precipitated by sulfide ion in alkaline solution. Like nickel sulfide, it is unusual in that it is not precipitated from acid solutions, but is not soluble, or only very slowly so, in dilute hydrochloric acid.

Sodium bicarbonate precipitates **cobaltous carbonate**,  $\text{CoCO}_3 \cdot 6\text{H}_2\text{O}$ , at room temperature, and the anhydrous compound at higher temperatures. Basic carbonates are formed by the alkali carbonates.

**Cobaltous cyanide**,  $\text{Co}(\text{CN})_2 \cdot 3\text{H}_2\text{O}$ , is but slightly soluble in water, but dissolves in excess of cyanide ion to form a complex **cobaltocyanide** ion,  $\text{Co}(\text{CN})_6^{-4}$ , which, however, is readily oxidized to the cobaltic complex.

Cobaltous oxide forms important pigments upon fusion

with certain negative oxides. **Smalt**, a deep blue pigment, is really a cobalt glass. **Cobalt blue** is largely cobalt aluminate with more or less zincate. **Cobalt green** is cobalt zincate, and **turquoise green** the same with some chromite.

**23. Cobaltic Compounds.**—Due to the powerful oxidizing nature of cobaltic ion (Par. 21), its simple salts are difficult to prepare. The **fluoride**,  $\text{CoF}_3$ , forms when the metal is heated with fluorine, and the **sulfate**,  $\text{Co}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , may be prepared by the electrolysis of cobaltous sulfate, followed by fractional crystallization. The sulfate forms **alums**. These, as well as the simple sulfate, are blue in color. Solutions of the fluoride and sulfate readily hydrolyze to the hydroxide,  $\text{Co}(\text{OH})_3$  (probably hydrous cobaltic oxide), which, when ignited in air, forms  $\text{Co}_3\text{O}_4$ .

**24. Complex Cobaltic Compounds.**—The cobaltic ion forms a remarkable number of complex ions in which it possesses a coordination number of six. These complex ions are more stable than the corresponding cobaltous ions. The reason is indicated by the following scheme which shows the number of electrons in the various orbitals:

	$3d$					$4s$	$4p$				$5s$
$\text{Co}^{++}$	( $\cdot\cdot$ )	( $\cdot\cdot$ )	( $\cdot$ )	( $\cdot$ )	( $\cdot$ )	( )	( )	( )	( )	( )	( )
$\text{Co}(\text{CN})_6^{-4}$	( $\cdot\cdot$ )	( $\cdot\cdot$ )	( $\cdot\cdot$ )	<div style="border: 1px solid black; padding: 2px; display: inline-block;"> (<math>\cdot\cdot</math>) (<math>\cdot\cdot</math>) (<math>\cdot\cdot</math>) (<math>\cdot\cdot</math>) (<math>\cdot\cdot</math>) (<math>\cdot\cdot</math>) </div>						( $\cdot\cdot$ )	
										OCTAHEDRAL BOND ORBITALS	

Thus  $\text{Co}(\text{CN})_6^{-4}$  has one electron in a higher  $s$  orbital, and this electron is readily lost to form  $\text{Co}(\text{CN})_6^{-3}$ .

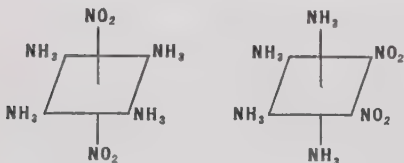
The formulae of the more important complexes with ammonia, halides, nitrite, and cyanide are given in Table X; and a few of the more familiar compounds are discussed below:

**Chloropentammine cobaltichloride**,  $\text{Co}(\text{NH}_3)_5\text{ClCl}_2$ , forms when an ammonical solution of cobaltous chloride is oxidized by air or hydrogen peroxide. As it is but slightly soluble in concentrated hydrochloric acid, the dark reddish-

violet compound is precipitated from the solution by the addition of this acid. The formation of this compound may be used to separate cobalt from nickel. The great stability of the complex is indicated by the fact that the ammonia is not removed by acid. Only two thirds of the chloride is precipitated by silver nitrate, but upon standing in contact with silver oxide it is converted into the hydroxide,  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{OH})_3$ ; and when this is dissolved in hydrochloric acid, the **aquapentammine cobaltichloride**,  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$ , is formed. This compound is not readily soluble in cold water. When the chloropentammine is heated under slight pressure with concentrated ammonia, the **hexammine cobaltichloride**,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , separates as orange-colored crystals.

**Potassium cobaltinitrite**, or potassium hexanitrocobaltate,  $\text{K}_3\text{Co}(\text{NO}_2)_6$ , is prepared by treating a cobaltous salt with potassium nitrite and acetic acid:  $\text{Co}^{++} + 3\text{K}^+ + 5\text{NO}_2^- + 2\text{HNO}_2 = \text{K}_3\text{Co}(\text{NO}_2)_6 + \text{NO} + \text{H}_2\text{O}$ . The potassium salt is but slightly soluble, and is sometimes employed as a pigment, cobalt yellow. The more soluble sodium salt is employed as a reagent in testing for potassium (cf. IV—25). The complex nitrite ion is decomposed by alkalis, forming the hydroxides, and by strong acids with the liberation of oxides of nitrogen.

A number of **dinitrotetrammine cobaltic salts** have been



prepared. These compounds exhibit isomerism, due to the two possible arrangements of the coordination groups.

Cobaltous ion in the presence of cyanide is readily oxidized, even by hydrogen ion to form the **cobalticyanide**,  $\text{Co}(\text{CN})_6^{---}$ . This ion is very stable, and like the corresponding ferricyanide, forms precipitates with ions of many of the heavier metals.

TABLE X  
COBALTIC COORDINATION COMPOUNDS

+ 3 Cation	Undissociated compounds
$[\text{Co}(\text{NH}_3)_6]\text{X}_3$	$[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$
$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{X}_3$	— 1 Anion
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{X}_3$	$\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$
+ 2 Cation	— 2 Anion
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{X}_2$	$\text{K}_2[\text{Co}(\text{NH}_3)(\text{NO}_2)_5]$
$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{X}_2$	— 3 Anion
$[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}, \text{Cl}]\text{X}_2$	$\text{K}_3[\text{Co}(\text{NO}_2)_6]$
+ 1 Cation	$\text{K}_3[\text{Co}(\text{CN})_6]$
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{X}$	
$[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{X}$	
$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{X}$	
$[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{X}$	

**25. Nomenclature of Complex Compounds.**—The following system of nomenclature has been proposed by Werner and is in general use:

(a) If the complex is a negative ion, the name of the positive ion is first.

(b) In giving the structure of the coordination complex, the following order is followed:

(1) Acid radical:  $\text{Cl}^-$ , chloro;  $\text{CO}_3^{--}$ , carbonato;  $\text{CNS}^-$ , thiocyanato;  $\text{NO}_2^-$ , nitro, etc.

(2) The water or oxygen groups:  $\text{H}_2\text{O}$ , aqua;  $\text{O}^{--}$ , oxo;  $\text{O}_2^{--}$ , peroxo;  $\text{OH}^-$ , hydroxo.

(3) The ammonia groups. Mono, di, tri, etc.—ammine, also called ammino.

(4) Name of positive element. If complex is a positive ion, the following endings are used: charge + 1, a; charge + 2, o; charge + 3, i; charge + 4, e. If complex is a negative ion, the termination, ate, is added.

(c) If the complex is a positive ion, the acid radicals not in the coordination group complete the name. Examples:

$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ —Chloropentammine cobaltichloride  
 $\text{K}_3[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$ —Potassium tetranitrodiammine cobaltate.

**26. Cobalt Dioxide and Cobaltites.**—Powerful oxidizing agents in alkaline solution, e.g. hypochlorite and hypoiodite, form the dioxide,  $\text{CoO}_2$ . The sesquioxide, which is prepared by igniting cobaltous nitrate, is generally considered to be the cobaltous cobaltite,  $\text{Co}(\text{CoO}_3)$ , as is also the tricobalt tetroxide,  $\text{Co}_3\text{O}_4$ , i.e.,  $2\text{CoO} \cdot \text{CoO}_2$ . Other cobaltites have been prepared by fusing cobaltous oxide with basic oxides in air, e.g.,  $\text{MgCoO}_3$ .

### NICKEL COMPOUNDS

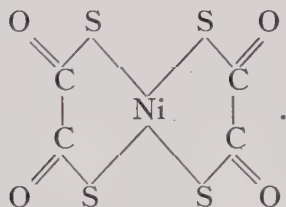
**27. Oxidation States.**—The principal oxidation state of nickel is + 2. No + 3 salts are known, and the + 3 hydroxide which is frequently mentioned in the literature appears to be the dioxide. The dioxide is slightly acidic, and a few salts of it have been prepared. There is some evidence for the formation of a + 1 oxide, and the + 1 cyanide complex ion,  $\text{Ni}(\text{CN})_3^{--}$ , is known. A few nickelates, i.e.  $\text{K}_2\text{NiO}_4$ , have been prepared. Potential values are summarized below:

	VOLTS <sub>25°</sub>
$\text{Ni} = \text{Ni}^{++} + 2e^-$ .....	+ 0.25
$\text{Ni}^{++} + 2\text{H}_2\text{O} = \text{NiO}_2 + 4\text{H}^+ + 2e^-$ .....	- 1.75
$\text{Ni} + 2\text{OH}^- = \text{Ni}(\text{OH})_2 + 2e^-$ .....	+ 0.66
$\text{Ni} + 6\text{NH}_3(\text{aq}) = \text{Ni}(\text{NH}_3)_6^{++} + 2e^-$ .....	0.48
$\text{Ni}(\text{OH})_2 + 2\text{OH}^- = \text{NiO}_2 + 2\text{H}_2\text{O} + 2e^-$ .....	- 0.49
$\text{Ni}^{++} + 4\text{H}_2\text{O} = \text{NiO}_4^{--} + 8\text{H}^+ + 4e^-$ .....	- 1.8

**28. Nickelous Compounds.**—Nickelous compounds are generally green or blue in color, and show many resemblances to cupric compounds. The **hydroxide**,  $\text{Ni}(\text{OH})_2$ , forms as a light green precipitate upon the addition of alkalis to a nickel solution. It is soluble in ammonium hydroxide, due to the formation of the complex nickel ammonia ion  $\text{Ni}(\text{NH}_3)_6^{++}$  which, like the corresponding cupric ion, has a deep blue color. The **oxide**,  $\text{NiO}$ , results from the direct union of the elements, or from the ignition of the hydroxide or the dioxide. The oxide and hydroxide are readily soluble in acids.



The **halides** are readily soluble, highly hydrated in water, and ammoniated in liquid ammonia solutions. The **bromide**,  $\text{NiBr}_2 \cdot 6\text{NH}_3$ , is precipitated by the addition of concentrated ammonia to a hot solution of nickel bromide. This property is sometimes utilized in the separation of nickel from cobalt. The **cyanide**,  $\text{Ni}(\text{CN})_2$ , is but slightly soluble in water, but dissolves in excess of cyanide, forming the **complex cyanide ion**,  $\text{Ni}(\text{CN})_4^{--}$ . It differs from the ferrous and cobaltous complex cyanides in that it cannot be oxidized to a nickelic compound, but it may be reduced to the + 1 complex,  $\text{Ni}(\text{CN})_3^{--}$ . The diamagnetic tetra-coordinated complexes of  $\text{Ni}^{++}$  are planar and not tetrahedral. The complex cyanide is an example, as is the thiooxalate.



The carbonyl,  $\text{Ni}(\text{CO})_4$  is tetrahedral and the same is true of the paramagnetic complex ions of  $\text{Ni}^{++}$ , e.g.,  $\text{Ni}(\text{H}_2\text{O})_4^{++}$  and  $\text{Ni}(\text{N}_2\text{H}_4)_2^{++}$ .

Below  $31^\circ$ , the **sulfate** crystallizes as the heptahydrate,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ . At higher temperature, two forms of hexahydrated salts are formed, one blue and the other green. **Nickel ammonium sulfate**,  $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , is used in nickel electroplating. The **nitrate**,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , is extremely soluble in water. Alkali carbonates precipitate nickel from solution as a basic carbonate, but the normal **carbonate**,  $\text{NiCO}_3 \cdot 6\text{H}_2\text{O}$ , may be precipitated from a solution containing an excess of carbonic acid.

**Nickel sulfide**,  $\text{NiS}$ , like cobalt sulfide, is not precipitated from acid solutions by hydrogen sulfide, but is precipitated from ammonia solutions, and the sulfide so formed does not dissolve in dilute hydrochloric acid. The sulfide appears

to exist in three modifications. The most soluble modification, which is first formed from alkaline solutions, quickly changes to a form which is less soluble, and also less rapidly soluble, in acid.

**29. Nickel Dioxide and Nickelites.**—Moderately strong oxidizing agents (Par. 27) in alkaline solution convert nickelous oxide into a hydrous oxide which may be a solid solution of  $\text{NiO}$  and  $\text{NiO}_2$ . With long oxidation the composition appears to approach that of  $\text{NiO}_2$ . This oxide is an extremely powerful oxidizing agent in acid solution, and readily evolves oxygen under these conditions. **Barium nickelite**,  $\text{BaNi}_2\text{O}_5$ , has been prepared by fusing the oxide with barium carbonate. Alkali peroxides form with nickelous salts an oxide of the same general formula as the dioxide, but its reactions indicate that it is the nickelous peroxide of + 2 nickel.

Hydrous nickel dioxide is the oxidizing constituent of the **Edison storage battery**. The cell reaction upon discharge may be represented by the equation:  $\text{Fe} + \text{NiO}_2 + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2 + \text{Ni}(\text{OH})_2$ . The electrodes are iron and nickel dioxide, and the electrolyte, sodium hydroxide. The potential of the cell is about 1.35 volts at  $20^\circ$ , and depends but slightly upon the concentration of hydroxide, since this substance enters into the cell reaction only so far as it affects the activity of the water. A similar battery employing cadmium instead of iron is in use in Europe. This cell has a potential of 1.2 volts.

**30. Analytical.**—In the systematic scheme for separation of the positive ions (Append. VI), cobalt and nickel are precipitated as sulfides by ammonium sulfide. In the separation from other members of this analytical group, advantage is taken of the slow solubility of the sulfides in cold dilute hydrochloric acid and the non-amphoteric character of the hydroxides. A number of procedures are employed in separating cobalt and nickel; the simplest probably being the precipitation of nickel by dimethylglyoxime,  $\text{HON}$

:  $\text{C}(\text{CH}_3)\text{C}(\text{CH}_3) : \text{NOH}$ , as  $\text{Ni}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$  from solutions containing acetate and acetic acid. Other methods of separation depend upon the slight solubility of nickel chloride in an ether-hydrogen chloride solution and upon the conversion of cobalt into its + 3 compounds, e.g. the precipitation of cobalt as potassium cobaltinitrite; the precipitation of the sesquioxide,  $\text{Co}_2\text{O}_3$ , by bromine in neutral solution; and the formation of chloropentammine cobaltichloride.

In gravimetric analysis nickel may be weighed as the nickel dimethylglyoxime, after drying at  $120^\circ$ ; as the oxide,  $\text{NiO}$ ; or as the metal after electrolytic precipitation. The electrolytic precipitation is made from an ammoniacal solution, and nickel and cobalt are deposited together.

Cobalt is often precipitated as potassium cobaltinitrite, and as the salt of nitroso-beta-naphtol,  $\text{Co}(\text{C}_{10}\text{H}_6\text{ONO})_3$ . In both procedures, it is weighed as the oxide,  $\text{Co}_3\text{O}_4$ .

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# Chapter XX

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## PLATINUM AND PALLADIUM METALS

1. The triads: ruthenium, rhodium, palladium; and osmium, iridium, platinum, bear the same relation to the second and third transition series that iron, cobalt, and nickel do to the first (cf. XIX).

The six elements of these two series are so similar in properties that the separation of the naturally occurring alloys into the pure metals is not simple, and the commercial term "platinum" generally refers to the whole group.

These elements differ from iron, cobalt, and nickel in their greater nobility, and in their even greater tendencies to form complex ions, or coordination compounds.

Although the similarities in the properties are very pronounced, there are, however, distinct changes in both the horizontal and vertical periodic relations, as is indicated in the following table of their oxidation states.

TABLE I  
OXIDATION STATES

Fe	2, 3, (4), 6	Co	2, 3, 4	Ni	(1), 2, (3), 4
Ru	2, 3, 4, 6, 7, 8	Rh	(1), (2), 3, 4, (6)	Pd	(1), 2, — 4, (6)
Os	(2), 3, 4, 6, (7), 8	Ir	(1), (2), 3, 4, 6	Pt	(1), 2, (3), 4, (6)

( ) Very unstable.

Among the more important of these relations which may be pointed out are: the similarity of the + 6 compounds of iron, ruthenium, and osmium to those of chromium, molybdenum, and tungsten; the similarity of nickel, palladium,

and platinum to copper, silver, and gold; the formation of volatile tetroxides by ruthenium and osmium; the remarkable absorption of hydrogen by nickel, palladium, and platinum, and the increasing tendency to form complex ammonia ions shown by the elements on the right.

**2. Occurrence.**—The important platinum ores are placer deposits in which the metal occurs as small grains or nuggets, the most extensive deposits being those in Russia, Colombia, and Transvaal. The nickel ores of Ontario contain small amounts of platinum as the mineral sperrylite,  $\text{PtAs}_2$ .

Crude native platinum generally contains all of the platinum metals. The following percentage compositions show the usual range: Pt, 60–80; Fe, 5–10; Pd, 1–2; Rh, 0.5–2; Ru, 0.5–2; Os, 1–10; Ir, 1–10. In addition, metal known as osmiridium is found, which contains largely osmium and iridium with small amounts of the other metals. The percentages of the elements in igneous rocks are extremely low, the approximate values being: Pt,  $10^{-9}$ ; Ir,  $10^{-10}$ ; Os,  $10^{-10}$ , Rh,  $10^{-11}$ , and Ru,  $10^{-11}$ .

**3. Metallurgy.**—Platinum is extracted from sand and gravel by washing and gravity concentration processes similar to those used with gold (cf. VII). For the separation of the crude metal into its constituents, it is usually first digested with aqua regia. This dissolves the greater part of the metal, but leaves a residue of any osmiridium, which is fused with zinc in order to render it soluble in acid. The separation of the various metals from the solution then becomes a matter of qualitative analysis (Par. 35).

**4. Properties and Uses of the Metals.**—The most important atomic and physical constants are summarized in Table II.

Ruthenium and osmium are grey like iron, while the other metals are more like silver. Rhodium is one of the whitest of all the metals. Osmium has the greatest density of any metal, is brittle, and hard enough to scratch glass.

Rhodium and iridium are a little softer, and palladium and platinum very malleable. When the metals are formed by the decomposition of their compounds at comparatively low temperatures, they are left in a finely divided or "spongy" condition. Hydrosols, or colloidal solutions, are readily prepared by striking an arc between electrodes of the metals under water.

TABLE II  
ATOMIC AND PHYSICAL PROPERTIES

	Ru	Rh	Pd	Os	Ir	Pt
Atomic weight . . . . .	101.7	102.91	106.7	190.8	193.1	195.23
Atomic number . . . . .	44	45	46	76	77	78
Isotopes . . . . .	96, 98, 99, 100, 101, 102, 104	101, 103	102, 104, 105, 106, 108, 110	186, 187, 188, 189, 190, 192	191, 193	192, 194, 195, 196, 198
Electrons in various quantum levels, 1st . . .	2	2	2	2	2	2
2d . . . . .	8	8	8	8	8	8
3d . . . . .	18	18	18	18	18	18
4th . . . . .	8 + 7	8 + 8	8 + 10	32	32	32
5th . . . . .	1	1		8 + 6	8 + 9	8 + 9
6th . . . . .				2		1
Density . . . . .	12.2	12.5	12.0	22.48	22.4	21.45
Melting point, ° C. . . . .	2450	1995	1555	2700	2350	1770
Boiling point, ° C. . . . .	> 2700	> 2500	2200	> 5300	4800	4400
Electrical resistivity, 20° C., ohm-cm. $\times 10^6$ . . . .	10	5.1	10.8	9	6	10.5
Ionization potentials . . . .	—	7.7	8.3	ca. 8.7	9.0	8.88

Spongy palladium and platinum, like nickel, show a remarkable catalytic effect upon many gas reactions. The use of platinum as a catalyst in the manufacture of sulfuric acid, ammonia, and nitric acid, has been mentioned. Platinum causes the instant explosion of a mixture of oxygen and hydrogen, or the ignition of alcohol vapor in air. An electrode coated with finely divided platinum, called platinum black, has a very low overvoltage for hydrogen and other gases, and is often employed in the construction



of electrical cells where a reversible gas electrode is desired. The platinum black surface may be prepared by the electrolytic precipitation of the metal from a chloroplatinate solution. Spongy platinum and palladium absorb large volumes of many gases, the absorption of hydrogen by the latter being especially remarkable (Par. 27).

The consumption of the platinum metals in the more important industries is given in Table III. Commercial platinum is usually alloyed with the harder metals, especially iridium and rhodium, to make it more durable. The average price per ounce in 1937 for the pure metals was ruthenium, \$30; rhodium, \$40; osmium, \$40; palladium, \$28; iridium, \$100; and platinum, \$50. However, the fluctuations in the prices are quite large.

TABLE III  
CONSUMPTION OF PLATINUM METALS IN U. S., 1937  
Values in Troy Oz.

	Pt	Pd	Ir	OTHERS
Jewelry.....	50,000	8,000	3,000	1,000
Dental.....	11,000	40,000	100	30
Electrical.....	10,000	20,000	10,000	350
Chemical.....	18,000	200	100	200

**5. Platinum,** due to its high melting point, incorrodibility, and malleability, is almost indispensable in the manufacture of chemical utensils for high temperature ignitions. Such ware, however, must be handled with some care since it is attacked by a number of reagents, e.g. aqua regia, chlorine solution, ferric chloride, and fused alkalis. It alloys with many metals, especially lead, tin, bismuth, and mercury; and unites with carbon, phosphorus, sulfur, and silicon, becoming brittle. However, alkali carbonates may be ignited in platinum crucibles without damage. Alloys of palladium and gold, such as “**palau,**” are employed to some extent as substitutes for platinum in chemical ware.

When pure platinum or platinum-iridium alloys are subjected to high temperature for a long period, appreciable loss of weight occurs, doubtless due to the formation of oxide. Platinum-rhodium alloys, however, are much less subject to such "volatilization." Platinum-iridium alloys are employed in the electrical industry in contact points.

**6. Reactions of the Metals.**—The more important reactions are summarized in Table IV. Reference should be made to the paragraphs dealing with the states of each element for approximate potential values. All of the metals exhibit "passivity" with strong oxidizing agents, so that they are not dissolved by as many reagents as the potential values would indicate. (See also Par. 5 for additional reactions of platinum.)

TABLE IV  
REACTIONS OF PLATINUM METALS

	Ru	Rh	Pd	Os	Ir	Pt
Spongy metal heated in oxygen	RuO <sub>2</sub> at 700–1200	Rh <sub>2</sub> O <sub>3</sub> slowly below 1150°	PdO slowly at 700°	OsO <sub>4</sub> at 200°	IrO <sub>2</sub> slowly at 1050°	PtO slowly at 450°
Spongy metal heated in chlorine	K <sub>2</sub> RuCl <sub>6</sub> when KCl is present	RhCl <sub>3</sub>	PdCl <sub>2</sub>	OsCl <sub>4</sub> at 700°	K <sub>2</sub> IrCl <sub>6</sub> when KCl is present	PtCl <sub>2</sub> at 360°
Hot HNO <sub>3</sub>	Insol.	Insol.	Slowly sol. Pd(NO <sub>3</sub> ) <sub>2</sub>	Insol.	Insol.	Insol.
Aqua regia	H <sub>2</sub> RuCl <sub>6</sub>	Very slowly soluble H <sub>3</sub> RhCl <sub>6</sub>	H <sub>2</sub> PdCl <sub>6</sub>	OsO <sub>4</sub>	Very slowly soluble H <sub>2</sub> IrCl <sub>6</sub>	H <sub>2</sub> PtCl <sub>6</sub>
Fused with KOH + KNO <sub>3</sub>	K <sub>2</sub> RuO <sub>4</sub>	RhO <sub>2</sub>	PdO	K <sub>2</sub> OsO <sub>4</sub>	Ir <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> PtO <sub>3</sub> •nH <sub>2</sub> O
Fused with KHSO <sub>4</sub>	Insol.	KRh(SO <sub>4</sub> ) <sub>2</sub>	PdSO <sub>4</sub>	Insol.	Ir <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Basic sulfate slowly at 250°

## RUTHENIUM COMPOUNDS

**7. Oxidation States.**—Ruthenium assumes an unusually large number of different oxidation states, 2, 3, 4, 6, 7, and

8. Compounds of the higher states in acid solutions are powerful oxidizing agents, and are reduced to salts of + 3 ruthenium. The metal is oxidized in alkaline solution to ruthenite,  $\text{RuO}_3^{--}$ , ruthenate,  $\text{RuO}_4^{--}$ , perruthenate,  $\text{RuO}_4^-$ , or the tetroxide  $\text{RuO}_4$  with the potential increasing for each step.

The following are approximate potentials for the more important couples:

	VOLTS <sub>25°</sub>
$\text{Ru} = \text{Ru}^{++} + 2e^-$ .....	- 0.45
$\text{Ru}^{++} + 5\text{Cl}^- = \text{RuCl}_5^{--} + e^-$ .....	- 0.3
$\text{RuCl}_5^{--} + \text{H}_2\text{O} = \text{RuCl}_5\text{OH}^{--} + \text{H}^+ + e^-$ .....	- 1.3
$\text{RuCl}_5\text{OH}^{--} + 3\text{H}_2\text{O} = \text{RuO}_4 + 5\text{Cl}^- + 7\text{H}^+ + 4e^-$ .....	- 1.5
$\text{Ru} + 6\text{OH}^- = \text{RuO}_3^{--} + 3\text{H}_2\text{O} + 4e^-$ .....	0.3
$\text{RuO}_3^{--} + 2\text{OH}^- = \text{RuO}_4 + \text{H}_2\text{O} + 2e^-$ .....	- 0.6

**8. The + 2 State.**—The fact that the oxide,  $\text{RuO}$ , does not appear to exist indicates that in alkaline solution this state is unstable, probably decomposing to give the metal and ruthenate (+ 6).

In acid solution, **halides** of  $\text{Ru}^{++}$  may be prepared by the reduction of the + 3 compounds by zinc, hydrogen sulfide, or by cathodic reduction. The solution has an azure blue color; solid **cesium ruthenium chloride**,  $\text{Cs}_3\text{RuCl}_5 \cdot 2\text{H}_2\text{O}$ , has been obtained from it, but the salt is rapidly oxidized in air.

**Potassium ruthenocyanide**,  $\text{K}_4\text{Ru}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ , is comparatively stable, and forms when ruthenium compounds of higher states are fused with potassium cyanide. It resembles ferrocyanide in the solubilities of its salts, and is oxidized by chlorine, probably to the + 3 cyanide.

**9. The + 3 State.**—The **chloride**,  $\text{RuCl}_3$ , is formed when the finely divided metal is oxidized by chlorine; the complex chloride,  $\text{K}_2\text{RuCl}_5$ , is readily prepared by the reduction of the + 4 complex, by alcohol, or other mild reducing agents.

The chloride in solution forms a bright red **ammonia**

**complex**, and with alkalis precipitates the hydrous oxide,  $\text{Ru}_2\text{O}_3$ , which is not soluble in excess of reagent.

The chloride forms a complex with nitric oxide,  $\text{RuCl}_3 \cdot \text{NO} \cdot \text{H}_2\text{O}$ , and a large number of **alkali complex chlorides** have been prepared, e.g.  $\text{K}_2\text{RuCl}_5\text{H}_2\text{O}$ ,  $\text{K}_2\text{RuNOCl}_5$ , and also the **nitrite**,  $\text{K}_2\text{Ru}(\text{NO}_2)_5$ .

The **bromide**,  $\text{RuBr}_3$ , is similar to the chloride in its reactions. The **iodide**,  $\text{RuI}_3$ , is but slightly soluble, and does not appear to form complex alkali iodides.

**10. The + 4 State.**—The dioxide,  $\text{RuO}_2$ , is obtained by heating the finely divided metal in air. It unites with metal oxides to form **ruthenites**, e.g.  $\text{BaRuO}_3$ . The **sulfate**,  $\text{Ru}(\text{SO}_4)_2$ , may be prepared by oxidizing the **sulfide**,  $\text{RuS}_2$ , with nitric acid or by heating the tetroxide with sulfuric acid. The free tetrachloride has not been prepared; but the potassium ruthenichlorides,  $\text{K}_2\text{RuCl}_6$  and  $\text{K}_2\text{RuCl}_5\text{OH}$ , form when potassium ruthenate is dissolved in cold dilute hydrochloric acid.

**11. The + 6 and + 7 States.**—**Potassium ruthenate**,  $\text{K}_2\text{RuO}_4 \cdot \text{H}_2\text{O}$ , forms when the metal is fused with potassium hydroxide and nitrate. It is soluble in water, forming a deep orange red solution. With cold dilute hydrochloric acid, the complex ruthenichloride is formed, but the **ruthenyl chloride**,  $\text{RuO}_2\text{Cl}_2$ , probably forms as an intermediate step. When acted on by chlorine at  $60^\circ$ , the solution becomes dark green through the formation of perruthenate,  $\text{RuO}_4^-$ . The alkali salts of the latter have been obtained as black crystals possessing a green metallic luster.

**12. Ruthenium Tetroxide.**—The tetroxide forms in small quantities by the action of oxygen upon finely divided metal, but is best prepared by the oxidation of an alkaline solution of ruthenate, or by the action of hot nitric acid and perchloric acids on compounds of the lower oxidation states. The oxide melts at room temperature to an orange liquid, decomposes around  $106^\circ$ , and unlike osmium tetroxide, it is not poisonous. It is somewhat soluble in water,

but the oxide seems to possess neither acidic nor basic properties to any marked degree. In acid solution, it is a powerful oxidizing agent.

### OSMIUM COMPOUNDS

**13. Oxidation States.**—Osmium resembles ruthenium in forming compounds of the positive oxidation states, 2, 3, 4, 6, and 8. In hydrochloric acid osmium may be present as  $\text{OsCl}_6^{-3}$ ,  $\text{OsCl}_6^{-}$ , or  $\text{H}_2\text{OsO}_5$ . The oxidation-reduction potentials are extremely complicated, since almost every negative ion gives a different complex ion with the lower states.

	VOLTS <sub>25°</sub>
$\text{Os} + 6\text{Cl}^- = \text{OsCl}_6^{-3} + 3e^-$ .....	— 0.6
$\text{OsCl}_6^{-3} = \text{OsCl}_6^{-} + e^-$ .....	— 0.85
$\text{OsCl}_6^{-} + 4\text{H}_2\text{O} = \text{OsO}_4 + 6\text{Cl}^- + 8\text{H}^+ + 4e^-$ .....	— 1.0
$\text{Os} + 4\text{OH}^- = \text{OsO}_2 + 2\text{H}_2\text{O} + 4e^-$ .....	— 0.15
$\text{OsO}_2 + 4\text{OH}^- = \text{OsO}_4^{-} + 2\text{H}_2\text{O} + 2e^-$ .....	— 0.1
$\text{Os} + 9\text{OH}^- = \text{HOsO}_5^- + 4\text{H}_2\text{O} + 8e^-$ .....	— 0.02

**14. The + 2 State.**—The **chloride**,  $\text{OsCl}_2$ , has been prepared by heating the trichloride at  $500^\circ$ , but neither it nor complex chlorides appear to have been prepared in solution. The slightly soluble iodide  $\text{OsI}_2$  is precipitated when iodide is added to  $\text{OsCl}_6^{-3}$ . It is claimed that the reduction of the tetroxide with sulfur dioxide yields the **sulfite**,  $\text{OsSO}_3$ ; and this, when heated, gives the **oxide**,  $\text{OsO}$ .

The **complex cyanides**, e.g.  $\text{K}_4\text{Os}(\text{CN})_6$ , are probably the most stable compounds of this state.

**15. The + 3 State.**—The chloride,  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ , has been prepared by reducing osmic acid with alcohol in the presence of chloride. When treated with sodium carbonate, the **sesquioxide**,  $\text{Os}_2\text{O}_3$ , is formed.

The following are some of the more important complex salts of this state:  $\text{K}_3\text{OsCl}_6$  (potassium chlorosmite),  $\text{K}_2\text{OsNOCl}_5$ ,  $\text{K}_2\text{Os}(\text{NO}_2)_5$ ,  $\text{KOs}(\text{NO})\text{O}_2$ . The latter com-

pound, called **potassium osmiamate**, is obtained by the action of ammonia on a cold alkaline solution of the tetroxide. It dissolves in hydrochloric acid to form the complex chloride.

**16. The + 4 state.**—Chlorine reacts with the metal at about  $700^{\circ}$  to form the **tetrachloride**,  $\text{OsCl}_4$ . It slowly hydrolyzes in water to the hydrrous **dioxide**,  $\text{OsO}_2$ .

Among the complex salts of this state are  $\text{K}_2\text{OsCl}_6$  (potassium chlorosmate),  $\text{K}_2\text{OsBr}_6$ ,  $\text{K}_2\text{OsI}_6$ , and  $\text{Na}_6\text{OsCl}_2(\text{SO}_3)_4$ .

**17. The + 6 State.**—The trioxide is not known, but the metal fused with potassium hydroxide and nitrate gives **potassium osmate**,  $\text{K}_2\text{OsO}_4$ , and this salt is also prepared by reducing an alkaline solution of this tetroxide with alcohol. It is unstable in acid solution. Barium osmate,  $\text{BaOsO}_4$ , is but slightly soluble. Some hexafluoride forms when fluorine is passed over the metal at  $250^{\circ}$ . It is decomposed by water.

Many complex **osmyl** ions have been prepared, e.g.  $\text{OsO}_2\text{Cl}_4^{--}$ ,  $\text{OsO}_2(\text{C}_2\text{O}_4)_2^{--}$ ,  $\text{OsO}_2(\text{NO}_2)_4^{--}$ ,  $\text{OsO}_3(\text{NO}_2)_2^{--}$ ,  $\text{OsO}_3\text{Cl}_2^{--}$ . None of the ions appear to be stable in acid solution.

**18. Osmium Tetroxide.**—The volatile **tetroxide**,  $\text{OsO}_4$ , is formed by direct combustion of the metal in air, or by its oxidation with hot concentrated nitric or sulfuric acids. The vapor has an odor resembling chlorine and is extremely poisonous. The oxide is soluble in water, but the solution is only very slightly acid ( $K_1$  for  $\text{H}_2\text{OsO}_5$  is  $8 \times 10^{-13}$ ). Alkalies form weakly bound compounds, e.g.  $\text{OsO}_4 \cdot 2\text{KOH}$ , which are readily soluble, and their solution is highly alkaline. As indicated in Par. 13, the oxide is a powerful oxidizing agent.

The **octafluoride**,  $\text{OsF}_8$ , and probably the **chloride**,  $\text{OsCl}_8$ , form in small amounts when the metal is heated in the halogen. These compounds are highly volatile and hydrolyze to the tetroxide in water.



## RHODIUM COMPOUNDS

**19. Oxidation States.**—Rhodium forms compounds having as positive oxidation states 1, 2, 3, 4, and 6. Of these the + 3 and + 4 are the more important. Unstable  $\text{Rh}_2\text{O}$  and  $\text{RhCl}$  have been prepared. The ion,  $\text{Rh}^{++}$ , is probably stable but in the presence of chloride is readily oxidized to  $\text{RhCl}_6^{-3}$ . Rhodic ion,  $\text{Rh}^{+++}$ , resembles cobaltic ion in the nature of its coordination compounds, and the dioxide is somewhat similar to cobalt dioxide.

	VOLTS 25°
$\text{Rh} = \text{Rh}^{++} + 2e^-$ .....	ca. - 0.6
$\text{Rh}^{++} = \text{Rh}^{+++} + e^-$ .....	ca. - 0.7
$\text{Rh}^{+++} + 2\text{H}_2\text{O} = \text{RhO}_2 + 4\text{H}^+ + e^-$ .....	ca. - 1.4
$\text{RhCl}_6^{-3} + 2\text{H}_2\text{O} = \text{RhO}_2 + 4\text{H}^+ + 6\text{Cl}^- + e^-$ .....	< - 1.4

**20. The + 3 State.**—The **oxide**,  $\text{Rh}_2\text{O}_3$ , results when the metal is heated in air below  $1150^\circ$ . Above that temperature, the oxide decomposes into the metal and oxygen. The hydrous oxide is precipitated from rhodium solutions by alkalies, and is somewhat soluble in excess of concentrated alkali, doubtless with the formation of **rhodites**.

The **trichloride**,  $\text{RhCl}_3$ , may be prepared by heating the metal in chlorine, and the salt so obtained is not soluble in water or acids. However, hydrated chloride formed by dissolving the sesquioxide in hydrochloric acid, is highly deliquescent. The **bromide**,  $\text{RhBr}_3$ , and **iodide**,  $\text{RhI}_3$ , have also been prepared. The latter is not readily soluble in hot water. The sulfate,  $\text{Rh}_2(\text{SO}_4)_3$ , forms alums. The **sulfide**,  $\text{Rh}_2\text{S}_3$ , is precipitated from acid solutions by hydrogen sulfide; but if excess of hydrogen sulfide is employed, the compound  $\text{Rh}_2\text{S}_3 \cdot 3\text{H}_2\text{S}$  appears to form, and normal sulfide precipitates but slowly.

The following coordination compounds are analogous to the corresponding cobalt compounds:  $\text{K}_3[\text{RhCl}_6]$ ,  $\text{Na}_2[\text{RhCl}_5\text{H}_2\text{O}]$ ,  $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$ ,  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ ,  $\text{K}_3[\text{Rh}(\text{CN})_6]$ , and  $\text{K}_3[\text{Rh}(\text{NO}_2)_6]$ .

**21. Rhodium Dioxide.**—Powerful oxidizing agents in alkaline solution, e.g.  $\text{ClO}^-$ , convert the sesquioxide into the **dioxide**,  $\text{RhO}_2$ . The dioxide is not soluble in water or alkalies, but dissolves in hydrochloric acid with the evolution of chlorine. Continued action of sodium hypochlorite on the dioxide gives a blue solution which is thought to contain **sodium rhodate**,  $\text{Na}_2\text{RhO}_4$ .

### IRIDIUM COMPOUNDS

**22. Oxidation States.**—The important oxidation states of iridium, like those of rhodium, are + 3 and + 4. Powerful oxidizing agents in alkaline solutions form iridates (+ 6), but these are not stable in acid.

The solid chlorides,  $\text{IrCl}$  and  $\text{IrCl}_2$ , are stable but decompose in the presence of water to the metal and the + 3 chloride.

	VOLTS <sub>25°</sub>
$\text{Ir} = \text{Ir}^{+++} + 3e^-$ .....	ca. - 1.0
$\text{Ir}^{+++} + 2\text{H}_2\text{O} = \text{IrO}_2 + 4\text{H}^+ + e^-$ .....	ca. - 0.7
$\text{Ir} + 6\text{Cl}^- = \text{IrCl}_6^{-3} + 3e^-$ .....	- 0.72
$\text{IrCl}_6^{-3} = \text{IrCl}_6^{-2} + e^-$ .....	- 1.02
$\text{IrO}_2 + 4\text{OH}^- = \text{IrO}_4^{--} + 2\text{H}_2\text{O} + 2e^-$ .....	> - 0.4

**23. The + 3 State.**—The **trichloride**,  $\text{IrCl}_3$ , forms when the finely divided metal is heated in chlorine. This product is not soluble in water, but the hydrated salt formed by dissolving the sesquioxide in hydrochloric acid is readily soluble. The chloride forms complex salts with the alkali chlorides, e.g.  $\text{K}_3\text{IrCl}_6$ ; similar compounds are formed by the **bromide** and **iodide**. These compounds are most readily prepared by reduction of the + 4 complex salts in acid solution. With alkalies, the **sesquioxide**,  $\text{Ir}_2\text{O}_3$ , is precipitated, and is soluble in excess of the reagent. With hydrogen sulfide in acid solution, the **sulfide**,  $\text{Ir}_2\text{S}_3$ , forms. Iridium **sulfate**,  $\text{Ir}_2(\text{SO}_4)_3$ , forms alums. Other important complex salts are the cyanide, e.g.  $\text{Na}_3\text{Ir}(\text{CN})_6$ , and **nitrites**, e.g.  $\text{K}_3\text{Ir}(\text{NO}_2)_6$ .

**24. The + 4 State.**—The **dioxide**,  $\text{IrO}_2$ , is obtained when the finely divided metal is heated to  $1100^\circ$  in air. A hydrated form results from the oxidation of the sesquioxide in air, from the addition of alkalis to the chloroiridates, and upon solution in water of alkali iridates. It is soluble in hydrochloric acid and in sulfuric acid, yielding the **chloride** and **sulfate** in solution. The solid chloride is a dark brown substance very soluble in water and forms stable **complex chlorides**, e.g.  $\text{K}_2\text{IrCl}_6$ . Hundreds of complex amines and halogen compounds are known.

**25. The + 6 state.**—Potassium **iridate**,  $\text{K}_2\text{IrO}_4$ , appears to be formed when the metal is fused with potassium hydroxide and nitrate, but oxygen is evolved when the salt is dissolved in water and the dioxide precipitated.

### PALLADIUM COMPOUNDS

**26. Oxidation States.**—The principal states of palladium, like platinum, are + 2 and + 4. There is some evidence for the formation of the monochloride upon heating the dichloride, but in general the + 2 compounds decompose directly into the metal at high temperatures. The trioxide  $\text{PdO}_3$  has been reported.

	VOLTS $25^\circ$
$\text{Pd} = \text{Pd}^{++} + 2e^-$ .....	— 0.83
$\text{PdCl}_4^{--} + 2\text{Cl}^- = \text{PdCl}_6^{--} + 2e^-$ .....	— 0.29
$\text{Pd} + 4\text{Cl}^- = \text{PdCl}_4^{--} + 2e^-$ .....	— 0.64
$\text{Pd} + 2\text{OH}^- = \text{Pd}(\text{OH})_2 + 2e^-$ .....	— 0.1

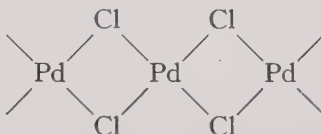
**27. Palladium and Hydrogen.**—Palladium absorbs hydrogen to a remarkable extent, 600 to 900 times its own volume at  $25^\circ$ , depending somewhat upon the physical condition of the metal. The pressure-concentration curves for the system indicate the formation of a solid solution of the metal and the hydride of empirical formula,  $\text{Pd}_2\text{H}$ ; the absorption is accompanied by a considerable increase in the volume of the metal. The gas is almost completely evolved, *in vacuo* at  $100^\circ$ . The hydrogenated metal is a good reducing

agent, e.g. reduces mercuric chloride and ferric salts, and also induces the oxidation by oxygen of many carbon compounds, possibly through the formation of hydrogen peroxide:  $\text{Pd}_4\text{H}_2 + \text{O}_2 = 4\text{Pd} + \text{H}_2\text{O}_2$ ; and  $\text{H}_2\text{O}_2 + \text{CO} = \text{H}_2\text{O} + \text{CO}_2$ .

**28. The + 2 State.**—The **halides** are formed by heating the metal in the halogen. The chloride,  $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ , is soluble in water, and with alkalis gives a precipitate of the hydrous oxide,  $\text{PdO}$ . This is soluble in concentrated ammonia, forming a **complex ammonia** ion, and upon dilution and acidifying slightly with hydrochloric acid, a precipitate of the diammoniate,  $\text{PdCl}_2 \cdot 2\text{NH}_3$ , is obtained. The **iodide**,  $\text{PdI}_2$ , and **cyanide**,  $\text{Pd}(\text{CN})_2$ , are but slightly soluble in water, but dissolve in excess of the precipitating ions. The **sulfide**,  $\text{PdS}$ , is precipitated from acid solutions by hydrogen sulfide. It is not soluble in ammonium sulfide. The **sulfate** and **nitrate** are readily soluble.

The following types of complex salts have been prepared:  $\text{K}_2[\text{PdCl}_4]$ ,  $\text{Ag}_2[\text{PdCl}_2 \cdot (\text{OH})_2]$ ,  $\text{K}_2[\text{Pd}(\text{CN})_4]$ ,  $\text{Na}_2[\text{Pd}(\text{NO}_2)_4]$ ,  $\text{K}_2[\text{PdBr}_2(\text{NO}_2)_2]$ ,  $[\text{PdCl}_2 \cdot 2\text{CO}]$ .

These tetra-coordinated complex ions are planar and not tetrahedral. The planar character of  $\text{Pd}^{++}$  is also illustrated by the crystal structure of the chloride  $\text{PdCl}_2$  in which infinite polymerization occurs to give strings of planar groups.



**29. The + 4 State.**—The hydrous dioxide,  $\text{PdO}_2 \cdot n\text{H}_2\text{O}$  is obtained by anodic oxidation of an acid solution of palladous nitrate. A precipitate of the **sesquioxide**,  $\text{Pd}_2\text{O}_3$ , probably  $\text{PdO} \cdot \text{PdO}_2$ , first forms but is decomposed by the acid leaving the dioxide. The dioxide decomposes around  $200^\circ$  to the monoxide.

The tetrachloride and bromide have not been prepared in

the pure state, but alkali complexes of the type  $M_2PdCl_6$  are known. The **potassium chloropalladate**,  $K_2PdCl_6$ , is prepared by the oxidation of the chloropalladite by chlorine, or by dissolving the dioxide in potassium chloride and hydrochloric acid. It is only slightly soluble in cold water and the same is true of the ammonium salt.

## PLATINUM COMPOUNDS

**30. Oxidation States.**—Platinum forms two important series of compounds corresponding to the oxidation states + 2 and + 4, and, in addition, a few comparatively unstable compounds of the + 1, + 3, and + 6 states. It exhibits strong tendencies to form coordination complexes; and the simple salts are, in general, either insoluble or slightly ionized in solution. For this reason, the oxidation-reduction potentials for the various oxidation changes depend very much upon the negative ion present.

	VOLTS <sub>25°</sub>
$Pt + 2H^+ + 4Cl^- = PtCl_4^{--} + 2e^-$ .....	- 0.73
$PtCl_4^{--} + 2Cl^- = PtCl_6^{--} + 2e^-$ .....	ca. - 0.72
$Pt = Pt^{++} + 2e^-$ .....	ca. - 1.2
$Pt + 4Br^- = PtBr_4^{--} + 2e^-$ .....	- 0.68
$Pt + 2OH^- = Pt(OH)_2^{--} + 2e^-$ .....	- 0.16
$Pt(OH)_2 + 4OH^- = Pt(OH)_6^{--} + 2e^-$ .....	ca. - 0.2
$Pt(OH)_6^{--} + 2OH^- = PtO_4^{--} + 4H_2O + 2e^-$ .....	- 0.4

**31. The + 2 State.**—**Platinous chloride**,  $PtCl_2$ , is generally prepared by heating the tetrachloride or chloroplatinic acid. It also forms when spongy platinum is heated in chlorine at 200°. It is not soluble in water, but dissolves in excess of hydrochloric acid to form a solution of **chloroplatinous acid**,  $H_2PtCl_4$ . This acid is most conveniently prepared, however, by the reduction of chloroplatinic acid by sulfur dioxide. The alkali and ammonium salts, e.g. potassium chloroplatinite,  $K_2PtCl_4$ , are soluble; but the silver and lead salts are not.

The chloride forms many addition compounds, for example,  $\text{PtCl}_2\text{CO}$  and  $\text{PtCl}_2\cdot\text{PCl}_3$ . The **fluoride** is **soluble**, but the **bromide** and **iodide** are not. The latter decompose readily:  $2\text{PtI}_2 = \text{Pt} + \text{PtI}_4$ .

**Platinous hydroxide**,  $\text{Pt}(\text{OH})_2$ , is prepared by boiling chloroplatinites with equivalent quantities of alkali. With excess of alkali, it decomposes, forming the metal and platinates. It is soluble in the halogen acids, but not in oxy-acids.

The black **sulfide**,  $\text{PtS}$ , precipitates when hydrogen sulfide is passed into a solution of chloroplatinite. It appears to be even less soluble than  $\text{HgS}$ .

The more important coordination compounds of + 2 platinum are given below. The **nitroplatinate**,  $\text{Pt}(\text{NO}_2)_4^{--}$ , is especially stable, as the platinum is not precipitated by alkalies or hydrogen sulfide, and strong acids form the nitro-acid,  $\text{H}_2\text{Pt}(\text{NO}_2)_4$ . Like  $\text{Ni}^{++}$  and  $\text{Pd}^{++}$ , these compounds have planar coordination instead of tetrahedral.

### Platino-coordination Compounds.

$\text{M}_2[\text{PtCl}_4]$	$\text{M}_2[\text{Pt}(\text{CN})_4]$	$[\text{PtCl}_2(\text{NH}_3)_2]$
$\text{M}_2[\text{PtBr}_4]$	$\text{M}_2[\text{Pt}(\text{CNS})_4]$	$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$
$\text{M}_2[\text{Pt}(\text{NO}_2)_4]$	$\text{M}[\text{PtCl}_3\cdot\text{NH}_3]$	$\text{M}[\text{Pt}(\text{CNS})_3\text{CO}]$

**32. The + 3 State.**—The trichloride may be formed at high temperatures. When warmed with hydrochloric acid the following decomposition occurs:  $2 \text{PtCl}_3 + 4\text{Cl}^- = \text{PtCl}_4^{--} + \text{PtCl}_6^{--}$ . There is some evidence for the sesquioxide  $\text{Pt}_2\text{O}_3$ . The complex cyanide ion  $\text{Pt}(\text{CN})_4^-$  is stable.

**33. The + 4 State.**—When platinum is dissolved in aqua regia, **chloroplatinic acid** is formed in solution; and upon removal of nitric acid by excess of hydrochloric acid, the hexahydrate,  $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$ , may be obtained by crystallization. The aqua regia solution also contains the **nitrosyl chloroplatinic chloride**,  $\text{PtCl}_4(\text{NO})_2\text{Cl}_2$ . By igniting the chloro-acid in an atmosphere of chlorine, the tetrachloride  $\text{PtCl}_4$ , is obtained. This salt is soluble in water, and



when heated to  $370^{\circ}$  decomposes:  $\text{PtCl}_4 = \text{PtCl}_2 + \text{Cl}_2$ . The **trichloride** probably forms as an intermediate step.

The chloroplatinates are the most important compounds of the metal. The silver and cesium salts are insoluble, and the rubidium, potassium, and ammonium only slightly soluble; hence these compounds are precipitated when the chloro-acid is treated with a solution of the corresponding positive ion.

**Platinum tetrabromide** and **iodide** are analogous to the chloride.

When the tetrachloride is heated with an excess of sodium hydroxide, **sodium platinate**,  $\text{Na}_2\text{Pt}(\text{OH})_6$ , is formed in solution; upon neutralizing this solution with acetic acid the hydrated dioxide,  $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$  or  $\text{H}_2\text{Pt}(\text{OH})_6$ , is precipitated. The oxide is soluble in the halogen acids, and in sulfuric acid gives a solution of the sulfate,  $\text{Pt}(\text{SO}_4)_2$ .

**Platinic sulfide**,  $\text{PtS}_2$ , is precipitated from acid solutions of the chloroplatinate by hydrogen sulfide. It is insoluble in nitric acid, but soluble in ammonium polysulfide.

Hundreds of complex **platiniammino-salts** are known in which platinum generally has the coordination number six. Examples of these complex types are:  $[\text{Pt}(\text{NH}_3)_6]\text{X}_4$ ,  $[\text{Pt}(\text{NH}_3)_4\text{X}_2]\text{X}_2$ , and  $[\text{Pt}(\text{NH}_3)\text{X}_5]\text{R}$ .

Nitroplatinites are oxidized by halogens with the formation of **tetranitro dihalidoplatinates**, e.g.  $\text{K}_2\text{Pt}(\text{NO}_2)_4\text{Cl}_2$ . Complex **platinithiocyanides**, e.g.  $\text{K}_2\text{Pt}(\text{CNS})_6$ , have been prepared; but the platinocyanides are oxidized to the + 3 and not the + 4 state, e.g.  $\text{AgPt}(\text{CN})_4$ .

**34. Perplatinate.**—In alkaline solution, the platينات are converted by anodic oxidation into perplatinate, e.g.  $\text{K}_2\text{PtO}_4$ . These compounds are decomposed by sulfuric acid, leaving an insoluble **trioxide**,  $\text{PtO}_3$ , which readily evolves oxygen upon heating.

**35. Analytical.**—The general principles of the scheme for the separation of the platinum metals, given by Gilchrist and Wichers, are as follows:

Osmium is removed as the tetroxide by distilling with nitric acid. The gas is absorbed in a solution of sulfur dioxide and hydrochloric acid. Ruthenium is next removed as the tetroxide by distillation after the addition of sulfuric acid and sodium bromate. The same absorbing agent is employed.

Rhodium, iridium, and palladium are precipitated and separated from platinum as the hydrous dioxides. The precipitation is made with sodium bicarbonate at about pH 6 from a chloride solution in the presence of sodium bromate. Platinum is precipitated from the filtrate after the addition of hydrochloric acid by saturating with hydrogen sulfide.

The dioxides of rhodium, iridium, and palladium are dissolved in hydrochloric acid and the palladium precipitated with dimethylglyoxime. The latter reagent is destroyed in the filtrate by evaporation with sulfuric acid and the rhodium precipitated as the metal by titanous chloride. The titanium which has been added may be removed with cupferron ( $\text{C}_6\text{H}_5\text{N}\cdot\text{NO}\cdot\text{ONH}_4$ ) and the iridium precipitated as the hydrous dioxide. After the isolation of the various elements, they are generally converted to the metal and weighed as such.

It is frequently necessary to separate gold from the platinum metal. This is readily accomplished by the precipitation of the metal from a 1.2*N* HCl solution by reduction with hydroquinone. The platinum metals remain in solution.

# Chapter XXI

## SCANDIUM, YTTRIUM, AND THE RARE EARTH ELEMENTS

1. Following barium, atomic number 56, there occurs a group of 15 remarkably similar elements known as the Rare Earths, which form + 3 ions resembling those of scandium and yttrium, the two preceding elements of Main Group III. The existence of this group was long a puzzling problem, as the older forms of the periodic table predicted but one element at this point. The explanation is now given in terms of the electronic structure of the atoms. The distribution of electrons in the various quantum levels in lanthanum, 57, and lutecium, 71, appears to be as follows:

Quantum level.....	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	6s	
Number of electrons	{ La ..	2	2	6	2	6	10	2	6	10		2	6	1	2
		2	2	6	2	6	10	2	6	10	14	2	6	1	2

Up to lanthanum, no electrons have gone into the 4f level, as the 5s, 5p, and 6s quantum levels represent lower energies since, in terms of the Bohr picture, electrons in these highly elliptical orbits are on the average closer to the nucleus. When these levels are occupied, the 4f levels then become the next most stable positions, and as 14 electrons are required to fill it, we find this group of 15 elements with the same number of outer or valence electrons, and differing only in the number of electrons in a level comparatively

deep within the kernel. The elements give up their  $5d$  and  $6s$  electrons fairly easily, and thus all form ions like  $\text{La}^{+++}$ .

The history of the rare earths dates from the discovery (about 1800) of two earth-like oxides which were given the names yttria and ceria. Further study of these oxides has resulted in the discovery of all the rare earth elements, although the final one, illinium, has not been isolated.

Although crude ceria and yttria generally contain at least traces of all the other rare earths, the former consists largely of the oxides of the elements of atomic numbers 57 to 62; and the latter of oxides of yttrium and the elements 63 to 71; these groups are generally designated as the **Cerium Subgroup** and the **Yttrium Subgroup**.

2. The rare earth elements are so similar that it is extremely difficult, in general, to separate two succeeding elements. There is, however, a gradual change in the properties in going from lanthanum to lutecium; for example, there is a slight decrease in the atomic volume and a corresponding slight decrease in the basic nature of the sesquioxide. Yttrium, being smaller than lanthanum, resembles the heavier members more than it does the lighter ones. Scandium is less basic than yttrium, and resembles aluminum more than the other elements do.

3. Since  $\text{La}^{+++}$ , with no  $f$  electrons, is especially stable, cerium tends to assume the same electron structure which it can do by forming a  $+4$  ion. Likewise, ytterbium tends to form the  $\text{Lu}^{+++}$  structure (completed  $f$  shell) and in addition to  $\text{Yb}^{+++}$  forms  $\text{Yb}^{++}$ . Gadolinium has one  $f$  electron in each of the seven  $f$  orbitals and  $\text{Gd}^{+++}$  is more stable than the  $+3$  ions of neighboring elements. Hence there is considerable tendency for europium to form  $\text{Eu}^{++}$  and terbium to form  $\text{Tb}^{+4}$ . It is interesting to note that the densities of europium and ytterbium (Table I) are out of line with the other rare earth metals and resemble more nearly those of the alkaline earth elements.

4. Compounds of most of the rare earths are highly magnetic (Table I). In completed electron shells, the orientation of the electron orbits appears to be such as to give zero resultant electrical moments, but this is not the case in uncompleted groups. Thus lanthanum ion,  $\text{La}^{+++}$ , and lutecium ion,  $\text{Lu}^{+++}$ , are not magnetic; but the transitional elements between are highly so.

TABLE I  
PROPERTIES OF SCANDIUM, YTTRIUM, AND THE RARE EARTH  
ELEMENTS

ATOMIC NUM- BER	NAME	SYM- BOL	ATOMIC WEIGHT	DEN- SITY	MELTING POINT	COLOR OF SALTS	MAGNETIC MOMENT (IN WEISS UNITS OF $M^{+++}$ )
21	Scandium . . . . .	Sc	45.10	(2.5)	1,200	Colorless	—
39	Yttrium . . . . .	Y	88.92	5.57	1,490	"	—
57	Lanthanum . . . . .	La	138.92	6.16	826	"	0
58	Cerium . . . . .	Ce	140.13	6.80	675	{ -ic orange -ous color- less	11.4
59	Praseodymium . . . . .	Pr	140.92	6.8	982	Green	17.8
60	Neodymium . . . . .	Nd	144.27	7.0	840	Red	18.0
61	Illinium . . . . .	Il	—	—	—	—	—
62	Samarium . . . . .	Sm	150.43	7.7	> 1300	Pink	8.0
63	Europium . . . . .	Eu	152.0	5.24		Rose	17.9
64	Gadolinium . . . . .	Gd	156.9	7.95		Colorless	40.0
65	Terbium . . . . .	Tb	159.2	8.33		"	47.1
66	Dysprosium . . . . .	Dy	162.46	8.56		Yellow	52.2
67	Holmium . . . . .	Ho	163.5	—		"	52.0
68	Erbium . . . . .	Er	167.2	9.16		Red	47.0
69	Thulium . . . . .	Tm	169.4	9.34		Green	35.6
70	Ytterbium . . . . .	Yb	173.04	7.01		Colorless	21.9
71	Lutecium . . . . .	Lu	175.0	9.74		"	0

5. Somewhat similar considerations apply to the colors of the rare earth compounds. Ions such as  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{La}^{+++}$ , and  $\text{Lu}^{+++}$ , which contain completed electron groups are colorless; while ions of such as  $\text{Cr}^{+++}$ ,  $\text{Co}^{++}$ , and most of the rare earths, which belong to transition groups, are generally colored. Characteristic absorption lines of the various elements in solutions of their compounds offer an easy method for their detection. The atomic emission spectra are readily excited in the electric arc.

**6. Occurrence.**—It is estimated that all the rare earths together constitute only  $1.5 \times 10^{-4}$  per cent of the igneous rocks. The order of decreasing abundance of the members of the group is given as: Ce, Nd, La, Y, Sm, Gd, Pr, Er, Yb, Lu, Dy, Ho, Tm, Tb, Eu, and Il. It may be observed from this order that the elements of odd atomic numbers are, in general, much less abundant than the even-numbered elements; and that the Yttrium Subgroup is less abundant than the Cerium Subgroup. The approximate percentage of scandium in the igneous rocks is  $10^{-7}$  and yttrium is probably somewhat more abundant.

The most important source of the Cerium Subgroup is the mineral **monazite**, which is essentially  $RPO_4$  (where R stands for any rare earth element), with generally 4 to 12 per cent of thorium phosphate. Although composed largely of cerium earths, it also contains a few per cent, 1 to 5, of the Yttrium Subgroup. Brazil and Travancore in India are the principal producers of the mineral, which is generally found in alluvial deposits or sands, where it has concentrated due to the high specific gravity of the particles. A phosphate, **xenotime**, which contains largely yttrium earths, also occurs.

**Gadolinite** is an yttrium silicate of the approximate formula,  $Be_2FeY_2Si_2O_{10}$ , and cerite is the cerium group silicate,  $H_3[Ca, Fe]Ce_3Si_3O_{10}$ . **Yttrocerite** is a rare earth with calcium fluoride, approximately  $RF_2 \cdot CaF_2$ , which contains about equal quantities of the two subgroups. Columbates and tantalates, such as **fergusonite**,  $(R)_2O_3[Cb, Ta]_2O_5$ , are found, often associated with thoria, zirconia, and uranates. Mineral carbonates also occur.

## PREPARATION AND PROPERTIES OF THE METALS

**7.** Due to the highly electropositive nature of the rare earths, the metals are difficult to prepare. The most satisfactory method is the electrolytic reduction of the oxide in



the molten fluoride. Reduction with sodium or magnesium generally gives an alloy.

An alloy of the metals of the cerium group is obtained from the rare earth residues of monazite sand, and is called **Misch metal**, or commercially "cerium." It is generally about 70 per cent cerium, and contains some iron. It is highly pyrophoric, i.e. gives sparks if scratched, especially if alloyed with iron, and is used extensively for cigar lighters, gas lighters, etc. During the World War, it was used in tracer bullets and luminescent shells.

The metals of the cerium group, except illinium, have been prepared in fairly pure form; but those of the yttrium group have not, as the higher melting points of these metals and the greater volatility of their chlorides render the electrolytic process difficult of operation.

The melting points and densities are given in Table I. The lower melting metals are about as soft as tin, but the higher melting ones resemble iron. The cerium metals tarnish readily in moist air and ignite when heated. Cerium has a kindling temperature of  $165^{\circ}$ , neodymium  $270^{\circ}$ , and lanthanum  $445^{\circ}$ . The most important reactions are summarized in Table II.

TABLE II  
REACTIONS OF RARE EARTH METALS

$4M + 3O_2 = 2M_2O_3$	
$2M + 6H_2O = 2M(OH)_3 + 3H_2$	Slow in cold
$2M + 3X_2 = 2MX_3$	X denotes halogen
$2M + N_2 = 2MN$	Forms with oxide when M burns in air
$M + 2C = MC_2$	At high temperature
$2M + 3S = M_2S_3$	
$2M + 3H_2 = 2MH_3$	Reaction at comparatively low temperature
$M = M_{(aq)}^{+++} + 3e^{-}$	La + 2.37

## COMPOUNDS

8. (a) **The + 3 State.**—Important solubility relations of the cerium and yttrium groups are summarized in Table III.

Lanthanum hydroxide is distinctly basic, and the hydroxides of the yttrium group, while less basic, do not dissolve in excess hydroxide. The sulfides, cyanides, simple sulfates, and halides, except fluorides, are all soluble.

**Scandium** forms a weaker base than any of the yttrium group, but resembles the cerium family in the slight solubility of the double potassium sulfate. Like aluminum, it forms a complex fluoride ion,  $\text{ScF}_4^-$ .

TABLE III  
PROPERTIES OF RARE EARTH COMPOUNDS

	CERIUM GROUP ELEMENTS 57 TO 62	YTTRIUM GROUP YTTRIUM AND ELEMENTS 63 TO 71
Hydroxides.....	Somewhat soluble in water	Slightly soluble in water
Carbonates.....	Not soluble in water nor $(\text{NH}_4)_2\text{CO}_3$ solution	Not soluble in water; soluble in $(\text{NH}_4)_2\text{CO}_3$ solution
Oxalates.....	Not soluble in water nor $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution	Not soluble in water; soluble in $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution
Fluorides.....	Not soluble	Not soluble
Potassium sulfates $\text{K}_3\text{R}(\text{SO}_4)_3$ .....	Not soluble in $\text{K}_2\text{SO}_4$ solution	Soluble in $\text{K}_2\text{SO}_4$ solution
Nitrates.....	Soluble in water; less soluble in $\text{HNO}_3$	Soluble in water; less soluble in $\text{HNO}_3$ , especially $\text{Gd}(\text{NO}_3)_3$
Basic nitrates.....	Somewhat soluble	Slightly soluble
Double nitrates, e.g., $\text{Mg}_3\text{R}(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ ...	Easily crystallized	Not readily crystallized
Phosphates $\text{RPO}_4$ .....	Not soluble	Not soluble
Formates.....	Slightly soluble	Moderately soluble

**9. (b) The + 4 State.**—Cerium forms a well defined series of + 4 compounds. In this state cerium is very similar to thorium, and the element is often considered as a member of the fourth periodic group.

**Cerium dioxide** is formed upon igniting cerous oxide. The hydrous oxide may be formed by the oxidation of cerous hydroxide in alkaline solution, or by the action of

alkalies upon ceric salts. It is soluble in nitric, sulfuric, and cold hydrochloric acids, giving the corresponding salts in solution. The chloride solution readily evolves chlorine upon heating. The **fluoride**,  $\text{CeF}_4 \cdot \text{H}_2\text{O}$ , is insoluble in water. It forms complex salts with the alkali fluorides. The **iodate**,  $\text{Ce}(\text{IO}_3)_4$ , is slightly soluble, resembling the thorium compound. Ceric ion is a powerful oxidizing agent. An accurate  $E^\circ$  value cannot be given as the activities are not known. In  $1M \text{ H}_2\text{SO}_4$  and equal concentration of  $\text{Ce}^{+++}$  and  $\text{Ce}^{++}$  the potential is  $-1.44$  and in nitric and perchloric acids, around  $-1.6$ . Ceric sulfate is a valuable volumetric reagent. In most respects it is very similar to permanganate but is not as highly colored so that the end-point must be determined by using either a spot plate reagent or an oxidizable dye.

Praseodymium, neodymium, and terbium all form dioxides (or solid solutions of  $\text{RO}_2$  in  $\text{R}_2\text{O}_3$ ) but they are even more powerful oxidizing agents than  $\text{CeO}_2$  and difficult to prepare pure.

**10. The + 2 State.**—Compounds of  $\text{Eu}^{++}$ ,  $\text{Yb}^{++}$ , and  $\text{Sm}^{++}$  are known, the potential of the couple,  $\text{Eu}^{++} = \text{Eu}^{+++} + e^-$  is  $0.43$  and the values for the corresponding couples for ytterbium and samarium appear to be about  $0.6$  and  $0.8$  respectively. Thus  $\text{Eu}^{++}$  is the only one of the ions which does not rapidly liberate hydrogen from water. It is readily prepared by the reduction of  $\text{Eu}^{+++}$  with zinc. The + 2 ions resemble  $\text{Ba}^{++}$  in the solubilities of their salts.

**11. Separation and Analyses.**—A fairly satisfactory method of separating scandium, thorium, and most of the members of the cerium subgroup is outlined in Table IV.

The complete separation of the neighboring elements of the yttrium rare earth group can be accomplished only by repeated fractional crystallization or precipitation. Thus, in the original separation of ytterbium and lutecium, 15,000 crystallizations were made.

The yttrium group is commonly divided into three sub-

TABLE IV

## ANALYSIS OF RARE EARTH GROUP

(From Noyes and Bray, *Qualitative Analysis for the Rare Elements*)

Precipitate of fluorides of Sc, †In, Th, RE. Extract with acid $\text{NH}_4\text{F}$			
Solution: $\text{NH}_4\text{ScF}_4$ Fume with $\text{H}_2\text{SO}_4$	Residue: RE, In, Th as fluorides Fume with $\text{H}_2\text{SO}_4$ , add water and $\text{NH}_4\text{OH}$ , filter out the precipitate, dissolve in $\text{HClH}_3\text{O}_2$ , pass in $\text{H}_2\text{S}$		
Precipitate: $\text{Sc}_2(\text{SO}_4)_3$ Add water and $\text{NH}_4\text{OH}$ , filter	Precipitate, yellow: $\text{In}_2\text{S}_3$	Filtrate: RE, Th, as acetates. Evaporate, add $\text{HNO}_3$ , $\text{KClO}_3$ , and $\text{KIO}_3$	
	Precipitate: $\text{Th}(\text{IO}_3)_4$ , Ce- $(\text{IO}_3)_4$ Add $\text{H}_2\text{O}_2$ , $\text{HNO}_3$ , and $\text{KIO}_3$	Filtrate: other RE Add $\text{NH}_4\text{OH}$ , filter, dissolve the precipitate in $\text{HCl}$ , add $\text{K}_2\text{CO}_3$	
	Residue $(\text{IO}_3)_4$ . Evaporate with $\text{HCl}$ , add $\text{H}_2\text{O}_2$	Precipitate: La, Pr, *Nd, *Sm, *Eu, and Y subgroup, all as $\text{KRE}(\text{CO}_3)_2$	Filtrate: Yttrium subgroup; and †Nd, †Sm, †Eu as $\text{KRE}(\text{CO}_3)_2$ . Add $\text{HCl}$ , then $\text{NH}_4\text{OH}$ , filter. Dissolve the precipitate in $\text{HCl}$ , evaporate, add $\text{HCHO}_2$ and $\text{NH}_4\text{CHO}_2$ .
	Precipitate, white: $\text{ThO}_2 \cdot \text{H}_2\text{O}_2$	Precipitate, orange: $\text{CeO}_2 \cdot \text{H}_2\text{O}_2$	Precipitate: Nd, Sm, Eu, †Y subgroup
			Fuse with $\text{NaNO}_3$ , extract with water, then with $\text{HClH}_3\text{O}_2$ and $\text{NaC}_2\text{H}_3\text{O}_2$ .
		Residue, brown: $\text{PrO}_2$ , †La $_2\text{O}_3$ , †Nd $_2\text{O}_3$	Water extract: *La †Nd †Sm Add $\text{NH}_4\text{OH}$ , filter heat precipitate with $\text{K}_2\text{CO}_3$ Acetate extract: *Nd *Sm †La †Pr Yttrium subgroup
		Precipitate: $\text{KL}_a(\text{CO}_3)_2$	Filtrate: Nd, Sm

\* A large part, but not all.

† A small fraction.

‡ All of the element when associated with certain other elements.

groups, and the members of each subgroup are usually separated as indicated below:

<i>Yttrium Group</i>	Terbium Subgroup	Eu	Separated by fractional crystallization of double sulfates and ethyl sulfates.
		Gd	
		Tb	
	Erbium Subgroup	Dy	Separated by fractional crystallization of ethyl sulfates and bromates.
		Ho	
		Er	
		Tm	
	Ytterbium Subgroup	Y	Separated by fractional crystallization of nitrates in nitric acid, bromates, or double ammonium oxalates.
		Yb	
		Lu	

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# Chapter XXII

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## THE RADIOACTIVE ELEMENTS

**1. The Atomic Nucleus.**—The ordinary chemistry of the elements is concerned almost entirely with those atomic properties which depend upon the valence electrons, and the only significance of the atomic nucleus is its positive charge which determines the number of orbital electrons or the atomic number. In this chapter a brief discussion will be given of the properties of the nucleus and their relation to transmutation reactions.

The radius of the nucleus increases from about  $2 \times 10^{-13}$  cm. for helium to about  $8 \times 10^{-13}$  cm. for uranium. The relation of volume to mass is that which would be expected for the close packing of some fundamental mass particle. Moreover, it was early observed that the atomic weights of the lighter elements, Table I, with oxygen taken as 16, were very close to whole numbers which suggested that the nucleus was an aggregate of particles. The assumption was first made that the nucleus was a condensed system of protons (hydrogen nuclei) and electrons. However, the discovery of the neutron (Par. 17) with approximately the mass of the proton and zero charge, has led to the more reasonable assumption that the nucleus consists of a close packing of protons and neutrons. Thus the  ${}^{16}_8\text{O}$  (nomenclature indicating atomic number 8 and mass 16) nucleus may be thought of as eight protons and eight neutrons. The decrease in mass ( $8 \times 0.0091 + 8 \times 0.0081 = 0.1476$ ) represents the binding energy of the nuclear particles.



TABLE I  
ATOMIC MASSES OF THE LIGHTER ELEMENTS

(These values are for  $O_{16} = 16$  instead of the chemical atomic weights which take the mixed oxygen isotopes = 16. The latter are obtained by dividing by 1.00023.)

NUCLEUS	ATOMIC MASS	NUCLEUS	ATOMIC MASS
${}^1_0\text{H}^1$	1.0091	${}^{12}_6\text{C}^{12}$	12.0036
${}^1_1\text{H}^1$	1.0081	${}^{13}_6\text{C}^{13}$	13.0073
${}^1_1\text{H}^2$	2.0147	${}^{14}_7\text{N}^{14}$	14.0073
${}^1_1\text{H}^3$	3.0171	${}^{15}_7\text{N}^{15}$	15.0048
${}^3_2\text{He}^3$	3.0171	${}^{16}_8\text{O}^{16}$	16.000
${}^4_2\text{He}^4$	4.0039	${}^{17}_8\text{O}^{17}$	17.0046
${}^6_3\text{Li}^6$	6.0167	${}^{18}_8\text{O}^{18}$	18.0056
${}^7_3\text{Li}^7$	7.0180	${}^{19}_9\text{F}^{19}$	19.0045
${}^8_4\text{Be}^8$	8.0078	${}^{20}_{10}\text{Ne}^{20}$	19.9986
${}^9_4\text{Be}^9$	9.0149	${}^{27}_{13}\text{Al}^{27}$	26.9909
${}^{10}_4\text{Be}^{10}$	10.0164	${}^{28}_{14}\text{Si}^{28}$	27.9860
${}^{10}_5\text{B}^{10}$	10.0161	${}^{29}_{14}\text{Si}^{29}$	28.9864
${}^{11}_5\text{B}^{11}$	11.0128		

Since 1 gram equals  $9 \times 10^{20}$  ergs or  $9.32 \times 10^8$  electron volts, this binding energy in  ${}^{16}_8\text{O}$  is 137 million electron volts. The reason that so many isotopes have atomic weights which are close to whole numbers arises through the fact that the mass contraction in the formation of the oxygen nucleus is an excellent mean value for a large number of elements.

**2. Radioactivity.**—For a given atomic number there is a limited range of the neutron to proton ratio for which the nuclei are stable. This range is greater for the elements of even atomic number than for those of odd and as a result the even atomic numbers have a larger number of isotopes. If the ratio is outside the stable range, nuclear reactions or radioactivity results. Thus if there is too large an excess of neutrons, electron emission or **beta-radiation** occurs. It is

not necessary to think of the electron as existing in the nucleus but rather that it is created by the conversion of a neutron into a proton, i.e., neutron equals proton plus electron. The loss of a beta-particle increases the atomic number by one and thus displaces the product to a periodic group one higher than the parent element.

If there is too large an excess of protons, a number of reactions may occur. With the heavier elements, an **alpha-particle** is emitted. This particle is the helium ( ${}_2\text{He}^4$ ) nucleus. Since it has a charge of  $+2$  the resulting atom occupies a position in the periodic system two groups lower than the parent. The alpha-particle is remarkably stable and in general the more abundant isotopes have mass numbers which are multiples of four, so it appears that the group of two protons and two neutrons must have some significance in the nuclear structure. Alpha-radioactivity often occurs with enormous energy, thus the  $\alpha$ -particle from thorium C' has an energy of 10.5 million e.v.

Another process which decreases the positive charge on the nucleus is the emission of a **positron**. This process is not known in the naturally occurring radioactive elements but frequently is observed in isotopes produced by bombardment (cf. Par. 18). The positron appears to be identical with the electron except for the opposite sign of the charge. The failure to observe the particle until recently was due to its short life in the presence of electrons; one positron and one electron react to form a photon or high energy (1.02 million e.v.) light ray, with their mutual annihilation. This process is reversible and the creation of a positron-electron pair from a high energy photon has been observed.

A third method by which the positive charge on a nucleus may be reduced is the reverse of  $\beta$ -radiation, that is, the capture of one of the inner orbital (K) electrons. This process is difficult to observe. It is known to happen in a number of the artificially produced radioactive isotopes

and may be taking place in some of the so-called stable isotopes.

The emission of particles from the nucleus is frequently accompanied by very high energy light rays, **gamma-rays**, which have higher frequencies than the hardest X-rays. The spectra of  $\alpha$ -rays often show several discrete energy groups corresponding to different quantum levels of the product nucleus. In this case the excess of energy in the excited product nucleus is emitted in the form of  $\gamma$ -radiation. The  $\beta$ -ray spectrum shows a continuous distribution of energy among the emitted electrons, terminating in a more or less sharp upper limit. Since the energies of the electrons from the nuclei are different but the energies of the initial and final nuclei are presumably the same, the question of the conservation of energy in the process is difficult to answer. The assumption is made that the energy must be taken away by some new kind of particle still escaping observation. This assumed particle is called the **neutrino**.

**3. The Transformation Series.**—The natural radioactive elements, except potassium, rubidium, lutecium and samarium, are all products of the disintegration of the two parent elements, uranium and thorium. The decomposition of these elements takes place in a series of alpha and beta steps, giving rise to the so-called uranium and thorium transformation series, the final product of each being an isotope of lead. A third series, the actinium series, also exists, which, like the others, ends with lead; but since uranium ores always contain actinium in constant ratio, it is assumed to be a branch of the uranium series, about 3 per cent of the uranium decomposing in this manner. Some of the radioactive elements undergo more than one type of disintegration, thus causing forking in the series. Table II gives the generic relations in the three series, and Table III summarizes some of the data relating to the members of the series.

**4. Radioactive Constants.**—The rate of decomposition is usually expressed by the fraction,  $\lambda$ , of a given quantity,  $Q$ , decomposed in a unit time,  $\lambda = (1/Q)(dQ/dt)$ . The average life,  $\theta$ , is  $1/\lambda$ , and the half period,  $T$ , i.e. the time required for the transformation of one half of a given quantity, is  $0.69\theta$ . If one element is decomposing to form a second element, which in turn decomposes into a third element, the number of atoms of the first and second elements,  $N_1$  and  $N_2$ , when a steady state is reached, is:  $N_1\lambda_1 = N_2\lambda_2$ . The velocity of the emitted rays is generally expressed relative to that of light, and their penetrating power in cm. of air, aluminum, or lead. An empirical relation of Geiger and Nuttall states that the logarithm of the average life is inversely proportional to the logarithm of the range of the alpha-particle in air for a given transformation series.

**5. Chemistry of the Radioactive Elements.**—The following paragraphs will present the more important facts pertaining to the chemical and physical properties of the naturally occurring radioactive elements.

**6.** The chemistry of uranium has been discussed in Chapter XVII. The ratio of abundance of UI to UII is about 2000 to 1. The isotope 235 which is present in somewhat larger amounts than UII is probably the parent of the actinium series.

**7.** Protoactinium is present in all uranium ores, about  $7 \times 10^{-8}$  g. per g. of uranium. As a member of Group V, it resembles its homologue tantalum, atomic number 52, in its chemical properties. A few tenths of a gram of the element in the form of oxide have been isolated. The pentoxide is somewhat more basic than the tantalum oxide. The chloride,  $\text{PaCl}_5$ , has been prepared and the oxide dissolves readily in HF. Salts such as  $\text{K}_2\text{PaF}_7$  may be crystallized from a solution. Like thorium the element may be precipitated as a peroxy-acid.

The very unstable uranium,  $\text{X}_2$ , also called brevium, may be separated from its parent element uranium  $\text{X}_1$  by taking

TABLE II  
TRANSFORMATION SERIES

Group . . . . .	3'	4'	5'	6'	7'	0	1	2	3	4	5	6
Atomic No..	81	82	83	84	85	86	87	88	89	90	91	92
										UX <sub>1</sub> ↗ UZ ↘ UX <sub>2</sub>		
										UX <sub>1</sub> ← UI		
										UX <sub>2</sub> ↘ UII		
										Io ← UII		
										UY ← AcU		
										Ac ← Pa		
										RdAc		
										MsThI ← Th		
										MsThII		
										RdTh		
										ThX ← RdTh		
										ThB ← ThA ← Tn ← ThX		
										ThC'' ← ThC		
										ThD ← ThC'		

advantage of the difference in properties of thorium and tantalum. Thus, the mixture treated with hydrogen fluoride forms the slightly soluble  $UX_1F_4$ , while the uranium  $X_2$  goes into solution, doubtless as the complex fluoride.

Uranium Z also appears to be a product of uranium  $X_1$ ,

TABLE III  
PROPERTIES OF THE RADIOACTIVE ELEMENTS

ATOMIC NUMBER	ELEMENT	MASS NUM- BER	HALF PERIOD	PARENT ELEMENT	RADIA- TION	DISINTE- GRATION ENERGY: ELECTRON VOLTS $\times 10^{-6}$
92	Uranium I	238	$4.5 \times 10^9$ yrs.		$\alpha$	4.05
92	Uranium II	234	$2 \times 10^6$ yrs.	UX <sub>2</sub>	$\alpha$	4.63
92	Ac Uranium	235			$\alpha$	
91	Protoactinium	231	$3 \times 10^4$ yrs.	UY	$\alpha$	5.01
91	Uranium X <sub>2</sub>	234	1.14 min.	UX <sub>1</sub>	$\beta$	2.32
91	Uranium Z	234?	6.7 hrs.	UX	$\beta$	—
90	Thorium	232.12	$1.39 \times 10^{10}$ yrs.		$\alpha$	4.23
90	Ionium	230	$7.6 \times 10^4$	UII	$\alpha$	4.54
90	Radiothorium	228	1.9 yrs.	MsThII	$\alpha$	5.33
90	Uranium X <sub>1</sub>	234	24.5 days	UI	$\beta$	0.13
90	Radioactinium	227	18.9 days	Ac	$\alpha$	6.05
90	Uranium Y	230?	25.5 hrs.	AcU	$\beta$	—
89	Actinium	227	18.4 yrs.	Pa	$\beta$	0.22
89	Mesothorium II	221	6.1 hrs.	MsThI	$\beta$	1.6
88	Radium	226	1,590 yrs.	Io	$\alpha$	4.79
88	Mesothorium I	228	6.7 yrs.	Th	$\beta$	0.05
88	Actinium X	223	11.2 days	RdAc	$\alpha$	5.7
88	Thorium X	224	3.6 days	RdTh	$\alpha$	5.68
86	Radon	222	3.8 days	Ra	$\alpha$	5.49
86	Thoron	220	54.5 sec.	ThX	$\alpha$	6.28
86	Actinon	219	3.9 sec.	AcX	$\alpha$	6.83
84	Polonium	210	136 days	RaE	$\alpha$	5.30
84	Radium A	218	3.05 min.	Rn	$\alpha$	6.11
84	Thorium A	216	0.14 sec.	Tn	$\alpha$	5.60
84	Actinium A	215	$2 \times 10^{-3}$	An	$\alpha$	7.36
84	Actinium C'	211	$10^{-3}$ sec.	AcC	$\alpha$	6.5
84	Radium C'	214	$10^{-4}$	RaC	$\alpha$	10.5
84	Thorium C'	212	$10^{-7}$ sec.	ThC	$\alpha$	10.5
83	Bismuth	201	Stable			
83	Radium E	210	4.85 days	RaD	$\beta$	1.22
83	Thorium C	212	60.8 min.	ThB	$\beta, \alpha$	$\beta$ 2.25, $\alpha$ 6.08
83	Radium C	214	19.5 min.?	RaB	$\beta, \alpha$	$\beta$ 3.15, $\alpha$ 5.5
83	Actinium C	211	2.16 min.?	AcB	$\alpha, (\beta)$	$\beta$ —, $\alpha$ 5.4
82	Radium G	206	Stable	Po	Rayless	—
82	Thorium D	208	Stable	ThC', ThC''	Rayless	—
82	Actinium D	207	Stable	AcC'', AcC'	Rayless	—
82	Radium D	210	25 yrs.	RaC', RaC''	$\beta$	0.035
82	Thorium B	212	10.6 hrs.	ThA	$\beta$	0.35
82	Actinium B	211	36.1 min.	AcA	$\beta$	0.30
82	Radium B	214	26.8 min.	RaA	$\beta$	0.65
81	Thallium	204.39	Stable		$\beta$	
81	Actinium C''	207	4.76 min.	AcC	$\beta$	1.40
81	Thorium C''	208	3.2 min.	ThC	$\beta$	1.79
81	Radium C''	210	1.3 min.	RaC	$\beta$	—



and to give uranium II by a beta decomposition, but these relations have not been definitely established.

8. The chemical properties of thorium have been discussed in Chapter XV. The isotopes cannot be separated by chemical means, but, for their preparation, advantage may be taken of their different parentage; thus ionium could be prepared free from thorium if a uranium ore free from the latter could be found. So far the purest sample of ionium prepared contains about 70 per cent thorium.

The separation of radiothorium from thorium may be made by frequently adding barium chloride and sulfuric acid to thorium solution over a period of 20 years. In this time, all of the original radiothorium will have disappeared, and the mesothorium I, which would form more radiothorium, is removed, as the sulfate.

Uranium Y is probably formed from actino-uranium.

9. Actinium is separated from uranium ores along with the rare earths, and its isolation from these elements is difficult, especially since its beta radiation is difficult to detect, and its presence cannot easily be determined until sufficient time has elapsed to build up its decomposition products. Like the rare earths, the potassium complex sulfate, the fluoride, and oxalate are slightly soluble, though the latter dissolves readily in dilute acids. It is not precipitated by hydrogen peroxide, as is thorium, nor by hydrogen sulfide. The hydroxide is more basic than lanthanum, is only partially precipitated by ammonium hydroxide, and dissolves readily in ammonium salts.

If it becomes possible to separate pure protoactinium, actinium may be readily obtained from this source.

The short life of mesothorium II leads to its presence only in extremely small quantities in thorium.

10. Radium and its isotopes are the heaviest members of the alkaline earth group, and as such, they are very similar in properties to barium. Radium sulfate is less soluble ( $2.1 \times 10^{-6}$  g. per 100 g. of water) than barium sul-

fate, and the hydroxide is more soluble. It is generally separated from barium by the fractional crystallization of the chlorides or bromides, the radium salts being the less soluble.

The commercial sources of radium are unaltered uranium minerals, such as pitchblende, largely  $\text{U}_3\text{O}_8$ , and carnotite,  $\text{K}_2\text{O}(\text{UO}_3)_2\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ . The radium content of the unaltered ores is about  $3.4 \times 10^{-7}$  g. per g. of uranium.

The process of extraction depends somewhat upon the type of mineral, but generally involves the precipitation of all the insoluble sulfates and the isolation of the barium and radium from this precipitate. This may be accomplished by reducing the sulfate to sulfide by carbon, dissolving the product in acid, and precipitating lead and other impurities by hydrogen sulfide. The first extraction of radium was carried out by M. and Mme. Curie. The principal source of radium at present is the rich uranium ores of the Belgian Congo, but recently discovered northern Canadian ores are assuming importance. One gram of radium emits  $3.7 \times 10^{10}$  alpha-particles per second. The energy is equivalent to 137 cal. per hour or a total heat for the whole life of the radium equal to the combustion of half a ton of coal.

Mesothorium I is a constituent of all thorium minerals, but its shorter life renders it less abundant, about  $3 \times 10^{-10}$  g. per g. of thorium. Since the thorium ores contain some uranium, radium is always present in the mesothorium. The commercial extraction from monazite is accomplished in a manner similar to that of radium. Mesothorium I changes to mesothorium II by a beta change, but the ray is very soft. However, the activity of the mesothorium decomposition products is such that a mesothorium preparation is 240 times more active than the same weight of radium.

Actinium X and thorium X are important only as sources of the very active decomposition products of the two series.

11. Radon, also called niton, or radium emanation; thoron, called thorium emanation; and actinon, called actinium emanation, are members of the noble gas family. The latter two, however, are too unstable to be of importance in themselves.

Radon melts at  $-71^{\circ}$ , and boils at  $-62^{\circ}$ . It is somewhat soluble in water, and very soluble in a number of organic liquids. Small quantities frequently occur in mineral waters. The volume of radon in equilibrium with 1 g. of radium is  $6.3 \times 10^{-3}$  cc. (this quantity is called 1 "curie").

12. Polonium, also called radium F, and its very unstable isotopes are members of Group VI, and hence resemble their homologue, tellurium. In acid solution, polonium forms the ion,  $\text{Po}^{++}$ , which is a rather powerful oxidizing agent:



Like lead ion, it may be deposited by anodic oxidation as the dioxide:



The dioxide has acid properties and appears to form salts of  $\text{PoO}_3^{--}$ . Polonium is precipitated by hydrogen sulfide, presumably as  $\text{PoS}$ , and there is evidence for the formation of a very unstable hydride,  $\text{PoH}_2$ .

Polonium is conveniently prepared from radium D or radiolead by fractional crystallization of the nitrates, or by the electrolytic reduction of the polonium.

The isotopes of polonium constitute part of the so-called "active deposits" formed by the disintegration of radon and its isotopes. They are usually collected by hanging negatively charged platinum foil in the gas. The extremely unstable C' elements are notable for their very penetrating alpha-particles.

**13.** The chemistry of bismuth is considered in Chapter XVI, and the chemical properties of its radioactive isotopes are doubtless the same. These isotopes may be separated from the "active deposit" (Par. 12) by taking advantage of decreasing ease of cathodic reduction from Subgroup VI to Subgroup IV. Simple heating of the active deposit on a platinum foil gives a partial separation, as the lead isotopes are more volatile than those of bismuth.

The "C" elements undergo both  $\beta$  and  $\alpha$  decomposition, the percentages of the  $\beta$  changes being RaC, 99.97; AcC, 0.2; ThC, 66.

**14.** Most uranium ores contain radium G mixed with ordinary lead, but the mineral curite gives pure radium G with an experimental atomic weight of 206.09, thus agreeing very closely with that predicted from the atomic weight of uranium. The purest thorium D which has been obtained from thorium minerals has an atomic weight of 207.9.

Radium D differs from the other two "D" elements in undergoing further decomposition. It has been isolated from radium preparations in barely visible quantities.

The "B" elements are present in the "active deposit" of the emanations, and may be separated by the greater volatility of their oxides, and by the fact that they are more electropositive than the isotopes of bismuth and polonium.

One g. of uranium in equilibrium with its products gives  $1.26 \times 10^{-10}$  g. of Pb<sub>206</sub> per year, and 1 g. of thorium  $4.8 \times 10^{-11}$  g. of Pb<sub>208</sub> per year. These figures are used in estimating the age of various minerals.

**15.** The very unstable isotopes of thallium may be isolated by collecting on a negative foil placed opposite a foil containing "active deposit" (Par. 12), since they are ejected from the deposit as the "recoil" product of the disintegration of the "C" elements. It is assumed that the product of their  $\beta$  disintegration is the same "D" element as is formed from the "C" elements.

16. Potassium, rubidium, and lutecium all show  $\beta$ -activity. The active isotopes are probably  $K^{40}$ ,  $Rb^{87}$ , and  $Lu^{176}$ . The upper energy limits of the rays in m.e.v. are 0.75, 0.137, and 0.215 respectively.

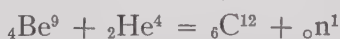
Samarium has a soft  $\alpha$ -ray activity, the range being 1.2 cm. in air and the calculated half-life  $7 \times 10^{11}$  years. It appears to be established that the neighboring rare earth neodymium has a weak  $\beta$ -activity.

17. **Artificial Disintegration.**—In 1919 Rutherford observed that the fast RaC  $\alpha$ -particles in passing through nitrogen gas occasionally (20 times per million  $\alpha$ -particles) produced a new long range particle which was identified as a proton. The mechanism of the process proved to be the nuclear reaction,



This experiment directed attention to the possibility of transmutation reactions and has led in recent years to the development of mechanisms for producing beams of high speed particles, especially protons and deuterons ( ${}_1\text{H}^2$  nuclei). The most important of these has been the Lawrence cyclotron. Hundreds of transmutation reactions have now been carried out and many new, highly unstable radioactive isotopes have been discovered.

The capture of the alpha-particle and the emission of a proton, illustrated above for nitrogen, occurs with many of the lighter elements,  $B^{10}$ ,  $F^{19}$ ,  $Ne^{23}$ ,  $Mg^{24}$ ,  $Mg^{25}$ ,  $Mg^{26}$ ,  $Al^{27}$ ,  $Si^{28}$ ,  $P^{31}$ , and  $S^{32}$ . However, in some cases (e.g.  $Li^6$ ,  $Li^7$ ,  $Be^9$ ,  $Be^{10}$ ,  $N^{14}$ ,  $F^{19}$ ,  $Na^{23}$ ,  $Mg^{24}$ ,  $Al^{27}$ , and  $P^{31}$ ) the capture results in the emission of the neutron.



This new particle had escaped detection because it produces no ionization along its path. Chadwick first deduced its presence from its ability to eject protons from material con-

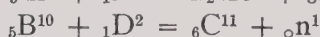
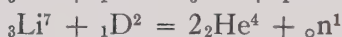
taining hydrogen. The neutron reacts with most nuclei and these reactions are considered below, Par. 19.

**18. Proton and Deuteron Transmutation.**—The proton and deuteron can penetrate the potential barrier of the positive nucleus much easier than the alpha-particle because of their smaller charge. The following are the more important transmutations produced by bombardment with high energy protons:



The first of these reactions is also shown by  $\text{Li}^6$ ,  $\text{N}^{14}$ ,  $\text{F}^{19}$ ,  $\text{Na}^{23}$ , and  $\text{K}^{39}$ .

Bombardment with deuterons leads to the following types of nuclear reactions,

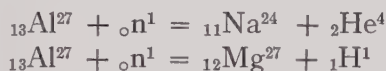


The first reaction is important as a source of neutrons. The fifth reaction is essentially the same, i.e., a proton is added to the  $\text{B}^{10}$  nucleus and a neutron liberated and similar reactions are found with  $\text{Be}^9$ ,  $\text{C}^{12}$ ,  $\text{N}^{14}$ ,  $\text{Na}^{23}$ , and  $\text{Al}^{27}$ . Reactions 2 and 3 result in the addition of a neutron to the nucleus and occur also with  $\text{Be}^9$ ,  $\text{B}^{10}$ ,  $\text{C}^{12}$ ,  $\text{N}^{14}$ ,  $\text{O}^{16}$ ,  $\text{Na}^{23}$ ,  $\text{Al}^{27}$ , and heavier elements. The formation of helium shown in the last equation is also given by  $\text{Al}^{27}$  and  $\text{N}^{14}$ .

**19. Neutron Reactions.**—Neutrons produced by the action of alpha-particles on beryllium or by the deuteron bombardments have kinetic energies generally of several



million electron volts. These fast neutrons, especially since they are uncharged, can readily penetrate into a nucleus, and are very effective in producing disintegrations by collision. The following equations illustrate the two most important nuclear reactions produced.



The first reaction with the neutron capture and the helium emission is given by a large number of elements, some of the more important being  $\text{Li}^6$ ,  $\text{B}^{10}$ ,  $\text{C}^{12}$ ,  $\text{N}^{14}$ ,  $\text{O}^{16}$ ,  $\text{F}^{19}$ ,  $\text{Ne}^{20}$ ,  $\text{P}^{31}$ ,  $\text{Cl}^{35}$ ,  $\text{Sc}^{45}$ ,  $\text{Mn}^{55}$ , and  $\text{Co}^{59}$ , and the second type of reaction by  $\text{Mg}^{24}$ ,  $\text{Si}^{28}$ ,  $\text{P}^{31}$ ,  $\text{S}^{32}$ ,  $\text{Ca}^{42}$ ,  $\text{Cr}^{52}$ ,  $\text{Fe}^{56}$ , and many of the heavier elements. There are also a few examples of neutron capture and deuteron emission and also cases where a fast neutron appears to knock out another neutron without capture. Most of the resulting nuclei are radioactive, and the properties of these artificial radioactive isotopes have been summarized in Table IV.

Since the neutron has approximately the same mass as the proton, elastic collisions with hydrogen atoms are very effective in reducing the speed of fast neutrons. About twenty collisions suffice to slow down (or cool off) the fast neutrons to the thermal energies of the hydrogen atom. Thus a few centimeters of water or paraffin at room temperature placed in the path of fast neutrons will slow them down from several million volts to an average energy of 0.03 volt. These slow neutrons are readily captured by a large number of nuclei forming isotopes with a mass one unit greater. As an example, thermal neutrons are captured by hydrogen, forming deuterium. The mean life of a neutron in paraffin is only  $1.7 \times 10^{-4}$  sec. From the data in Table I it is evident that the capture by  $\text{H}^1$  results in a decrease in mass and this energy is emitted in the form of  $\gamma$ -radiation. Among the more important cases of neutron capture are those by  $\text{C}^{12}$ ,  $\text{Na}^{23}$ ,  $\text{Mg}^{26}$ ,  $\text{Al}^{27}$ ,  $\text{Si}^{30}$ ,  $\text{Cl}^x$ ,  $\text{K}^{41}$ ,

$V^{51}$ ,  $Mn^{55}$ ,  $Cu^x Ga^x$ ,  $As^{75}$ ,  $Se^x$ ,  $Br^x Cd^x$ ,  $In^x$ ,  $Sb^x$ ,  $I^{27}$ ,  $Ba^{138}$ ,  $Hf^{180}$ ,  $W^x$ ,  $Re^x$ ,  $Ir^x$ , and  $Au^x$ . Uranium also captures a neutron forming a  $\beta$ -emitting isotope. The product of this activity must be element 93, but as yet it has not been isolated. However, the most extraordinary reaction of uranium and also thorium with neutrons is the so-called **nuclear fission**, in which the nucleus breaks into two more or less equal fragments. These fragments having atomic weights in the neighborhood of 100 to 140 are highly radioactive, giving off numerous beta-particles. The total energy emitted in the fission is around 200 million electron volts.

**20. Disintegration by  $\gamma$ -radiation.**—Gamma-radiation from  $ThC''$  has an energy of 2.6 m.e.v. and is capable of producing neutron emission from  $H^2$  and  $Be^9$ , the resulting isotopes being  $H'$  and  $Be^8$ . Proton bombardment of  $Li^7$  forming  $Be^8$  produces a 17 m.e.v.  $\gamma$ -ray. This radiation ejects neutrons from many atoms.

**21. Properties of Radioactive Isotopes.**—The development of the cyclotron has made available radioactive isotopes of many of the lighter elements. Since the Geiger counter detects the emission of single  $\beta$ - or  $\alpha$ -particles, a small amount of a radioactive isotope added to the stable isotope enables one to follow the course of the elements in chemical reactions. This application of the radioisotopes as indicators or "atom tags" has opened up extensive fields of investigation in almost every branch of chemistry.

TABLE IV  
SUMMARY OF RADIOACTIVE ISOTOPES

Table prepared by Dr. G. T. Seaborg

*Notation.*  $\beta^-$ , electron;  $\beta^+$ , positron;  $\alpha$ , alpha particle;  $\gamma$ , gamma radiation; s, second; m, minute; h, hour; d, days; y, year; K, electron capture. Energy in m.e.v.

NUCLEUS	RADIATION	HALF-LIFE	ENERGY OF PARTICLE
$^1\text{H}^3$	$\beta^-$	ca 150 d.	0.02
$^2\text{He}^6$	$\beta^-$	0.8 s.	3.7
$^3\text{Li}^8$	$\beta^-, \alpha$	0.88 s.	12 ( $\beta^-$ )
$^4\text{Be}^7$	K, $\gamma$	43 d.	
$^5\text{B}^{12}$	$\beta^-$	0.22 s.	12
$^6\text{C}^{11}$	$\beta^+$	20.5 m.	1.15
$^7\text{N}^{13}$	$\beta^+, \gamma$	9.93 m.	0.92, 1.20
$^7\text{N}^{16}$	$\beta^-$	8 s.	6.0
$^8\text{O}^{15}$	$\beta^+$	126 s.	1.7
$^8\text{O}^{19}$	$\beta^-$	31 s.	
$^9\text{F}^{17}$	$\beta^+$	70 s.	2.1
$^9\text{F}^{18}$	$\beta^+$	112 m.	0.7
$^9\text{F}^{20}$	$\beta^-$	12 s.	5.0
$^{10}\text{Ne}^{19}$	$\beta^+$	20.3 s.	2.20
$^{10}\text{Ne}^{23}$	$\beta^-$	40 s.	
$^{11}\text{Na}^{22}$	$\beta^+$	3.0 y.	0.58
$^{11}\text{Na}^{24}$	$\beta^-, \gamma$	14.8 h.	1.4
$^{12}\text{Mg}^{23}$	$\beta^+$	11.6 s.	2.82
$^{12}\text{Mg}^{27}$	$\beta^-, \gamma$	10.2 m.	1.8
$^{13}\text{Al}^{26}$	$\beta^+$	7.0 s.	2.99
$^{13}\text{Al}^{28}$	$\beta^-, \gamma$	2.4 m.	3.3
$^{13}\text{Al}^{29}$	$\beta^-$	6.7 m.	2.5
$^{14}\text{Si}^{31}$	$\beta^-$	170 m.	1.8
$^{15}\text{P}^{30}$	$\beta^+$	2.55 m.	3.6
$^{15}\text{P}^{32}$	$\beta^-$	14.30 d.	1.69
$^{16}\text{S}^{31}$	$\beta^+$	26 m.	
$^{16}\text{S}^{35}$	$\beta^-$	88 d.	0.107
$^{17}\text{Cl}^{34}$	$\beta^+$	33 m.	2.5
$^{17}\text{Cl}^{38}$	$\beta^-, \gamma$	37 m.	4.8
$^{18}\text{A}^{39} (?)$	$\beta^-$	4 m.	
$^{18}\text{A}^{41}$	$\beta^-, \gamma$	110 m.	2.7
$^{18}\text{A}^{37} (?)$		1.1 h.	
$^{19}\text{K}^{38}$	$\beta^+, \gamma$	7.7 m.	2.3
$^{19}\text{K}^{42}$	$\beta^-$	12.4 h.	3.5
$^{19}\text{K}^{43, 44}$	$\beta^-$	18 m.	
$^{20}\text{Ca}^{39} (?)$	$\beta^+$	4.5 m.	
$^{20}\text{Ca}^{49}$	$\beta^-, \gamma$	2.5 h.	2.3
$^{20}\text{Ca}^{45}$	$\beta^-, \gamma$	18.0 d.	0.2, 0.9
$^{21}\text{Sc}^{42}$	$\beta^+$	13.4 d.	1.4
$^{21}\text{Sc}^{43}$	$\beta^+$	4 h.	1.3
$^{21}\text{Sc}^{44}$	$\gamma$	52 h.	

TABLE IV (Cont'd)

NUCLEUS	RADIATION	HALF-LIFE	ENERGY OF PARTICLE
$^{21}\text{Sc}^{44}$	$\beta^+$	4 h.	1.6
$^{21}\text{Sc}^{46}$	$\beta^-, \gamma, K$	85 d.	0.26
$^{21}\text{Sc}^{47}$	$\beta^-, \gamma$	63 h.	1.1
$^{21}\text{Sc}^{48}$	$\beta^-, \gamma$	44 h.	0.6, 1.3
$^{21}\text{Sc}^{49}$	$\beta^-$	57 m.	1.8
$^{22}\text{Ti}^{51}$	$\beta^-, \gamma$	2.9 m.	
$^{22}\text{Ti}^{51}$	$\beta^-, \gamma$	72 d.	0.36
$^{23}\text{V}^{47}$	K	600 d.	
$^{23}\text{V}^{48}$	$\beta^+, K, \gamma$	16 d.	1.0
$^{23}\text{V}^{49}$	$\beta^+$	33 m.	1.9
$^{23}\text{V}^{50}$	$\beta^+$	3.7 h.	
$^{23}\text{V}^{52}$	$\beta^-$	3.9 m.	
$^{24}\text{Cr}^{51}$	K, $\gamma$	27 d.	
$^{25}\text{Mn}^{51}$	$\beta^+$	46 m.	2.0
$^{25}\text{Mn}^{52}$	$\beta^+, \gamma$	21 m.	2.2
$^{25}\text{Mn}^{52}$	$\beta^+, \gamma, K$	6.5 d.	0.7
$^{25}\text{Mn}^{54}$	K, $\gamma$	310 d.	
$^{25}\text{Mn}^{56}$	$\beta^-, \gamma$	2.59 h.	1.2
$^{26}\text{Fe}^{53}$	$\beta^+$	8.9 m.	2.9
$^{26}\text{Fe}^{55}$	K	> 1 y.	
$^{26}\text{Fe}^{59}$	$\beta^-, \gamma$	47 d.	0.4, 0.9
$^{27}\text{Co}^{56}$	$\beta^+, \gamma$	18.2 h.	1.50
$^{27}\text{Co}^{56}$	K, $\gamma$	240 d.	
$^{27}\text{Co}^{58}$	$\beta^+$	70 d.	
$^{27}\text{Co}^{60}$	$\beta^-, \gamma$	7 y.	0.16, 1.5
$^{27}\text{Co}^{58, 60}$	$\beta^-$	11 m.	
$^{28}\text{Ni}^{57}$	$\beta^+$	36 h.	0.67
$^{28}\text{Ni}^{63}$	$\beta^-, \gamma$	2.6 h.	1.9
$^{29}\text{Cu}^{58, 60}$	$\beta^+$	81 s.	
$^{29}\text{Cu}^{58, 60}$	$\beta^+$	7.9 m.	
$^{29}\text{Cu}^{61}$	$\beta^+$	3.4 h.	0.9
$^{29}\text{Cu}^{62}$	$\beta^+, K$	10.5 m.	2.8
$^{29}\text{Cu}^{64}$	$\beta^-, \beta^+, K$	12.8 h.	0.57 ( $\beta^-$ ), 0.66 ( $\beta^+$ )
$^{29}\text{Cu}^{66}$	$\beta^-$	5 m.	2.9
$^{30}\text{Zn}^{63}$	$\beta^+$	38 m.	2.3
$^{30}\text{Zn}^{65}$	$\beta^+, K, \gamma$	250 d.	0.4 ( $\beta^+$ )
$^{30}\text{Zn}^{69}$	$\gamma$	13.8 h.	
$^{30}\text{Zn}^{69}$	$\beta^-$	57 m.	1.0
$^{31}\text{Ga}^{64}$	$\beta^+$	48 m.	
$^{31}\text{Ga}^{65}$	K	15 m.	
$^{31}\text{Ga}^{66}$	$\beta^+$	9.4 h.	3.1
$^{31}\text{Ga}^{67}$	K, $\gamma$	83 h.	
$^{31}\text{Ga}^{68}$	$\beta^+$	68 m.	1.9
$^{31}\text{Ga}^{70}$	$\beta^-$	20 m.	5.0
$^{31}\text{Ga}^{72}$	$\beta^-, \gamma$	14 h.	2.6
$^{32}\text{Ge}^{69}$	$\beta^+$	29 m.	
$^{32}\text{Ge}^{71}$	$\beta^+$	37 h.	1.0

TABLE IV (*Cont'd*)

NUCLEUS	RADIATION	HALF-LIFE	ENERGY OF PARTICLE
$^{32}\text{Ge}^{69, 81}$		195 d.	
$^{32}\text{Ge}^{75, 77}$	$\beta^-$	81 m.	
$^{32}\text{Ge}^{75, 77}$	$\beta^-$	8 h.	
$^{33}\text{As}^{71, 73} (?)$	$\beta^-$	50 h.	
$^{33}\text{As}^{71, 73} (?)$	$\beta^+$	88 m.	
$^{33}\text{As}^{74}$	$\beta^-, \beta^+$	17 d. ( $\beta^-$ )	1.2 ( $\beta^-$ ), 0.9 ( $\beta^+$ )
$^{33}\text{As}^{76}$	$\beta^-, \gamma$ ; $\beta^+, K$	26 h.	1.1, 1.7, ( $\beta^-$ ) 0.7, ( $\beta^+$ )
$^{33}\text{As}^{77}$	$\beta^-, \gamma$	55 d.	
$^{33}\text{As}^{78}$	$\beta^-$	65 m.	
$^{34}\text{Se}^{75}$		48 d.	
$^{34}\text{Se}^{79, 81}$	$\beta^-$	57 m.	
$^{34}\text{Se}^{79, 81}$	$\beta^-$	19 m.	
$^{34}\text{Se}^{83}$	$\beta^-$	30 m.	
$^{34}\text{Se}$		sev. h.	
$^{34}\text{Se}$		sev. d.	
$^{35}\text{Br}^{78}$	$\beta^+$	6.4 m.	2.3
$^{35}\text{Br}^{80}$	$\gamma$	4.4 h.	
$^{35}\text{Br}^{80}$	$\beta^-, \gamma$	18 m.	2.0
$^{35}\text{Br}^{82}$	$\beta^-, \gamma$	34 hr.	0.7
$^{35}\text{Br}^{83}$	$\beta^-$	140 m.	1.05
$^{35}\text{Br}^{>82}$		40 m.	
$^{35}\text{Br}^{>82}$		22 h.	
$^{35}\text{Br}^{>82}$		3.8 h.	
$^{36}\text{Kr}^{79, 81}$		18 h.	
$^{36}\text{Kr}^{83}$	$\gamma$	112 m.	.035
$^{36}\text{Kr}^{85, 87}$	$\beta^-$	74 m.	
$^{36}\text{Kr}^{85, 87}$	$\beta^-$	4.5 h.	
$^{36}\text{Kr} (?)$		1-2 m.	
$^{36}\text{Kr}^{88}$	$\beta^-$	3 h.	
$^{37}\text{Rb}^{82, 84}$	$\beta^+$	1.5 m.	
$^{37}\text{Rb}^{82, 84}$	$\beta^+$	9.8 m.	
$^{37}\text{Rb}^{88}$	$\beta^-$	18 m.	
$^{37}\text{Rb}^{86, 88}$	$\beta^-$	18 d.	
$^{38}\text{Sr}^{87}$	$\gamma$	2.7 h.	
$^{38}\text{Sr}^{89}$	$\beta^-$	55 d.	1.9
$^{38}\text{Sr}^{>90}$		8-10 h.	
$^{38}\text{Sr}^{>90}$		ca 20 d.	
$^{38}\text{Sr}^{>90}$		> 20 d.	
$^{38}\text{Sr}^{>90}$	$\beta^-$	7 m.	
$^{38}\text{Sr}^{>90}$	$\beta^-$	6 h.	
$^{39}\text{Y}^{88}$	$\beta^+$	2.0 h.	1.2
$^{39}\text{Y}^{90}$	$\beta^-$	60 h.	2.6
$^{39}\text{Y}$	$\beta^-$	70 h.	1.3
$^{39}\text{Y}^{>90}$		3.5 h.	
$^{39}\text{Y}$		14 h., 80 h.	
		80 d.	

TABLE IV (Cont'd)

NUCLEUS	RADIATION	HALF-LIFE	ENERGY OF PARTICLE
$^{90}\text{Zr}$	$\beta^+$	70 h.	1.0
$^{90}\text{Zr}$	$\beta^-$	17-40 h.	1.25
$^{90}\text{Zr}$ (?)		10-30 m.	
$^{90}\text{Zr}$ (?)	$\beta^-$	2.5-5 h.	
$^{90}\text{Zr}$ (?)	$\beta^-$	90 m.	
$^{91}\text{Cb}$		4 m., 12 m.	
		38 m., 21 h.,	
		96 h.	
$^{92}\text{Cb}$	$\beta^-$	11 d.	1.0
$^{94}\text{Cb}$	$\beta^-$	7.5 m.	
$^{93}\text{Mo}$ (?)		7 h.	
$^{91, 93}\text{Mo}$	$\beta^+$	17 m.	1.8
$^{99, 101}\text{Mo}$	$\beta^-, \gamma$	67 h.	1.5
$^{101}\text{Mo}$	$\beta^-$	24 m.	1.3
$^{96}\text{Zr}$	$\beta^+$	2.7 h.	
$^{99, 101}\text{Zr}$	$\gamma$	6.6 h.	
$^{93}\text{Zr}$	K	90 d.	
$^{93}\text{Zr}$	K, $\gamma$	62 d.	
$^{93}\text{Zr}$	K (?), $\gamma$	110 h.	0.6
$^{93}\text{Zr}$	$\beta^-, \gamma$	55 m.	2.5
$^{93}\text{Zr}$	$\beta^-$	36.5 h.	
$^{93}\text{Zr}$	$\beta^-$	18 s.	
$^{93}\text{Zr}$	K	2 d.	
$^{95}\text{Ru}$		20 m.	
$^{103}\text{Ru}$	$\beta^-$	4 h.	
$^{105}\text{Ru}$	$\beta^-$	20 h.	
$^{97}\text{Ru}$ (?)	$\beta^-$	39 h.	
$^{97}\text{Ru}$ (?)		11 d.	
$^{97}\text{Ru}$ (?)		90 m.	
$^{104}\text{Rh}$	$\gamma$	4.2 m.	
$^{104}\text{Rh}$	$\beta^-$	44 s.	2.25
$^{105}\text{Rh}$	$\beta^-$	46 d.	
$^{95}\text{Rh}$		3 h.	
$^{95}\text{Rh}$		10.7 h.	
$^{95}\text{Rh}$		3 d.	
$^{107, 109}\text{Pd}$	$\beta^-$	13 h.	1.03
$^{111}\text{Pd}$	$\beta^-$	73 m.	
$^{102}\text{Ag}$		17 m.	
$^{104}\text{Ag}$ (?)	K	45 d.	
$^{106}\text{Ag}$	$\beta^+$	24.5 m.	2.04
$^{106}\text{Ag}$	K, $\gamma$	8.2 d.	1.2
$^{108}\text{Ag}$	$\beta^-$	2.3 m.	2.8
$^{110}\text{Ag}$	$\beta^-, \gamma$	22 s.	2.8
$^{108, 110}\text{Ag}$	$\beta^-$	225 d.	
$^{111}\text{Ag}$	$\beta^-$	7.5 d.	
$^{112}\text{Ag}$	$\beta^-, \gamma$	3.2 h.	2.2
$^{107, 109}\text{Cd}$	K, $\gamma$	6.7 h.	



TABLE IV (Cont'd)

NUCLEUS	RADIATION	HALF-LIFE	ENERGY OF PARTICLE
$^{109}\text{Cd}$	$\beta^+$	33 m.	
$^{116}\text{Cd}$	$\beta^-, \gamma$	2.5 d.	1.11
$^{117}\text{Cd}$	$\beta^-$	3.75 h.	
$^{118}\text{Cd}$	$\gamma$	50 m.	
$^{110}\text{In}$	$\beta^+$	65 m.	1.6
$^{110}\text{In}$	$\beta^+, \gamma$	20 m.	2.15
$^{112}\text{In}$	$\beta^-$	72 s.	
$^{112}\text{In}$	$\beta^-, \gamma$	2.7 d.	1.73
$^{113}\text{In}$	$\gamma$	105 m.	
$^{114}\text{In}$	$\beta^-, \gamma$	48 d.	1.75
$^{115}\text{In}$	$\gamma$	4.1 h.	
$^{116}\text{In}$	$\beta^-$	13 s.	2.8
$^{116}\text{In}$	$\beta^-, \gamma$	54 m.	0.85
$^{117}\text{In}$	$\beta^-, \gamma$	2.1 h.	1.73
$^{113}\text{Sn}$	K, $\gamma$	100 d.	
$^{126}\text{Sn}$	$\beta^-$	40 m.	
$^{126}\text{Sn}$	$\beta^-$	26 h.	
$^{126}\text{Sn}$	$\beta^-$	10 d.	
$^{126}\text{Sn}$		400 d.	
$^{125}\text{Sn}$	$\beta^-$	9 m.	
$^{119}\text{Sn}$	$\beta^-$	25 m.	
$^{119}\text{Sn}$	$\beta^-$	3 h.	
$^{119}\text{Sn}$	$\beta^-$	13 d.	
$^{119}\text{Sb}$	$\beta^-$	3.5 m.	
$^{120}\text{Sb}$	$\beta^+$	17 m.	1.53
$^{122}\text{Sb}$	$\beta^-$	2.8 d.	1.64
$^{124}\text{Sb}$	$\beta^-$	60 d.	1.8
$^{126}\text{Sb}$	$\beta^-$	3 h.	
$^{126}\text{Sb}$		ca 45 d.	
$^{126}\text{Sb}$		ca 2 y.	
$^{127}\text{Sb}$	$\beta^-$	80 h.	
$^{129}\text{Sb}$	$\beta^-$	4.2 h.	
$^{116, 119}\text{Sb}$	$\beta^+$	5 m.	
$^{131}\text{Sb}$	$\beta^-$	< 10 m.	
$^{131}\text{Sb}$	$\beta^-$	5 m.	
$^{121}\text{Te}$	K	120 d.	
$^{127}\text{Te}$	$\gamma$	90 d.	
$^{127}\text{Te}$	$\beta^-$	10 h.	
$^{129}\text{Te}$		30 d.	
$^{129}\text{Te}$	$\beta^-$	70 m.	
$^{131}\text{Te}$		30 h.	
$^{131}\text{Te}$	$\beta^-$	25 m.	
$^{131}\text{Te}$	$\beta^-$	43 m.	
$^{131}\text{Te}$	$\beta^-$	60 m.	
$^{131}\text{Te}$	$\beta^-$	77 h.	
$^{124}\text{I}$	$\beta^+$	4.0 d.	
$^{126}\text{I}$	$\beta^-, \gamma$	13.0 d.	1.1

TABLE IV (*Cont'd*)

NUCLEUS	RADIATION	HALF-LIFE	ENERGY OF PARTICLE
$^{53}\text{I}^{128}$	$\beta^-, \gamma$	25 m.	1.2, 2.1
$^{53}\text{I}^{130}$	$\beta^-, \gamma$	12.6 h.	0.83
$^{53}\text{I}^{131}$	$\beta^-, \gamma$	8.0 d.	0.69
$^{53}\text{I}^{>131}$	$\beta^-$	2.4 h.	
$^{53}\text{I}^{>131}$	$\beta^-$	54 m.	
$^{53}\text{I}^{>131}$	$\beta^-$	22 h.	
$^{54}\text{Xe}^{139}$	$\beta^-$	< 0.5 m.	
$^{54}\text{Xe}^{>139}$	$\beta^-$	ca 15 m.	
$^{54}\text{Xe}$		4.5 d.	
$^{54}\text{Xe}$		9 h.	
$^{55}\text{Cs}^{134}$		1.5 h.	
$^{55}\text{Cs}^{134}$		ca 1 y.	
$^{55}\text{Cs}^{139}$	$\beta^-$	6 m.	
$^{55}\text{Cs}^{>139}$	$\beta^-$	33 m.	
$^{56}\text{Ba}^{139}$	$\beta^-$	86 m.	
$^{56}\text{Ba} (?)$		3 m.	
$^{56}\text{Ba}^{>139}$	$\beta^-$	300 h.	
$^{56}\text{Ba}^{>140}$	$\beta^-$	14 m.	
$^{56}\text{Ba}^{>140}$	$\beta^-$	< 1 m.	
$^{57}\text{La}^{138} (?)$		2.2 h.	
$^{57}\text{La}^{140}$	$\beta^-$	31 h.	0.8
$^{57}\text{La}^{>140}$	$\beta^-$	ca 2.5 h.	
$^{57}\text{La}^{>140}$	$\beta^-$	< 30 m.	
$^{57}\text{La}^{>139}$	$\beta^-$	36 h.	
$^{58}\text{Ce}^{139} (?)$	$\beta^+$	2.1 m.	
$^{58}\text{Ce}^{141, 143}$		15 d.	0.12
$^{59}\text{Pr}^{140, 142}$	$\beta^+$	3.5 m.	
$^{59}\text{Pr}^{142}$	$\beta^-$	18.7 h.	
$^{60}\text{Nd}^{147}$	$\beta^-$	84 h.	
$^{60}\text{Nd}^{149}$	$\beta^-$	2.0 h.	
$^{60}\text{Nd}^{151}$	$\beta^-$	21 m.	
$^{61}\text{61} (?)$	$\beta^-$	12.5 h.	
$^{62}\text{Sm}$	$\beta^-$	21 m.	
$^{62}\text{Sm}$	$\beta^-$	46 h.	
$^{63}\text{Eu}^{152, 154}$	$\beta^-, \gamma$	9.2 h.	1.88
$^{63}\text{Eu}^{150}$	$\beta^+$	27 h.	
$^{63}\text{Eu}^{152, 154}$	$\beta^-, \gamma$	ca 1.2 y.	0.8
$^{64}\text{Gd}^{159, 161}$		8 h.	
$^{65}\text{Tb}^{160}$	$\beta^-$	3.9 h.	
$^{66}\text{Dy}^{165}$	$\beta^-$	2.5 h.	1.9
$^{66}\text{Dy} (?)$	$\beta^+$	2.2 m.	
$^{67}\text{Ho}^{164} (?)$	$\beta^-$	47 m.	
$^{67}\text{Ho}^{166}$	$\beta^-$	35 h.	1.6
$^{68}\text{Er}^{165} (?)$	$\beta^+$	1.1 m.	
$^{68}\text{Er}^{169, 171}$		7 m.	
$^{68}\text{Er}^{169, 171}$	$\beta^-$	12 h.	
$^{69}\text{Tm}^{170}$		105 d.	

TABLE IV (Cont'd)

NUCLEUS	RADIATION	HALF-LIFE	ENERGY OF PARTICLE
$^{70}\text{Yb}^{175, 177}$		3.5 h.	
$^{71}\text{Lu}^{177}$		4 h.	
$^{71}\text{Lu}^{177}$		6 d.	
$^{72}\text{Hf}^{181}$	$\beta^-$	55 d.	
$^{73}\text{Ta}^{180}$		14-21 m.	
$^{73}\text{Ta}^{180}$	$\text{K}, \gamma, \beta^- (?)$	8.2 h.	< 0.5
$^{73}\text{Ta}^{182}$	$\beta^-$	97 d.	
$^{74}\text{W}^{185, 187}$		23 h.	
$^{75}\text{Re}^{186}$	$\beta^-$	90 h.	1.2
$^{75}\text{Re}^{188}$	$\beta^-$	18 h.	2.5
$^{76}\text{Os}^{191, 193}$	$\beta^-$	40 h.	
$^{77}\text{Ir}^{192, 194}$	$\beta^-$	1.5 m.	
$^{77}\text{Ir}^{192, 194}$	$\beta^-$	19 h.	2.2
$^{77}\text{Ir}^{192, 194}$	$\beta^-$	60 d.	
$^{78}\text{Pt}^{197}$	$\beta^-$	18 h.	
$^{78}\text{Pt}^{197}$	$\beta^-$	3.3 d.	
$^{78}\text{Pt}^{199}$	$\beta^-$	31 m.	
$^{79}\text{Au}^{196}$	$\beta^-$	13 h.	
$^{79}\text{Au}^{196}$	$\beta^-$	4-5 d.	
$^{79}\text{Au}^{198}$	$\beta^-, \gamma$	2.7 d.	0.8
$^{79}\text{Au}^{199}$	$\beta^-$	3.3 d.	
$^{80}\text{Hg}^{197}$	$\text{K}, \gamma$	43 m.	< 0.4
$^{80}\text{Hg}^{203, 205}$		25 h.	
$^{81}\text{Tl}^{200} (?)$		4 m.	
$^{81}\text{Tl}^{200} (?)$		3.8 h.	
$^{81}\text{Tl}^{204, 206}$	$\beta^-$	4 m.	
$^{81}\text{Tl}^{204, 206}$	$\beta^-$	97 m.	
$^{82}\text{Pb}^{209}$	$\beta^-$	3.0 h.	
$^{82}\text{Pb}^{205}$		80 m.	
$^{83}\text{Bi}^{210}$	$\beta^-$	5 d.	
$^{84}\text{Po}^{210}$	$\alpha$	136 d.	
$^{90}\text{Uy}^{231}$	$\beta^-$	24.5 h.	
$^{90}\text{Th}^{233}$	$\beta^-$	26 m.	
$^{91}\text{Pa}^{233} (?)$	$\beta^-$	25 d.	
$^{92}\text{U}^{239}$	$\beta^-$	23 m.	



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# Glossary

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**ACID.**—A substance which gives hydrogen ion in solution, or which neutralizes bases yielding water. In general, an acid is a molecule with a positive field which is capable of neutralizing a basic molecule having a “free” electron pair.

**ACTIVITY.**—Cf. Appendix IV.

**ALLOTROPY.**—The property shown by certain elements of being capable of existence in more than one form, due to differences in the arrangement of atoms or molecules. (See Monotropic and Enantiotropic.)

**ALPHA-PARTICLES.**—Doubly charged helium atoms shot off during one type of radioactive change.

**AMPERE.**—Unit of electric current strength; one coulomb per second; the international ampere is the current which deposits 0.0011180 g. of silver per second.

**ÅNGSTROM UNIT.**— $10^{-10}$  meters;  $10^{-8}$  cm.

**ANGULAR MOMENTUM.**—Product of the angular velocity and moment of inertia. The latter is analogous to the mass in simple translation. Unit expressed in g. cm.<sup>2</sup>/sec.

**ANHYDRIDE (of acid or base).**—An oxide which when combined with water gives an acid or base.

**ANODE.**—The electrode at which oxidation occurs.

**ATMOSPHERE.**—Unit of pressure. Defined as pressure exerted by a column of mercury 76 cm. high;  $1.01325 \times 10^6$  dynes per cm.<sup>2</sup>; 14.7 lb. per sq. inch.

**ATOM.**—The unit particle of an element. A nucleus of definite integral positive charge surrounded by electrons.

**ATOMIC NUMBER.**—The net positive charge on the nucleus of an atom; the ordinal number of an atom in the periodic system.

**ATOMIC WEIGHT.**—Weight of an atom referred to the oxygen atom as 16.000.

**AVOGADRO'S NUMBER.**—The number of molecules in a mole;  $6.061 \times 10^{23}$ .

AVOGADRO'S RULE.—Equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules (approximately).

BAR.—Unit of pressure;  $= 10^6$  dyne cm.<sup>2</sup>; one atmosphere  $= 1.013$  bar.

BASE.—A substance which gives hydroxide ion in solution, or which neutralizes acids, yielding water.

BASE ELEMENT.—An easily oxidized element, as opposed to a noble element.

BOILING POINT.—The temperature at which the vapor pressure of a liquid reaches standard atmospheric pressure.

BRITISH THERMAL UNIT (BTU).—Heat required to raise 1 lb. of water 1° F.

CALORIE.—Unit of energy. Small calorie (denoted by cal.) is heat required to raise 1 g. of water 1° C. kcal.  $= 1000$  cal. Value varies with temperature. 1 cal. (15° C.)  $= 4.183$  joules.

CATALYST.—A substance which by its presence alters the rate of a reaction and itself remains unchanged at the end of the reaction.

CATHODE.—The electrode at which reduction occurs.

CATHODE RAYS.—A stream of electrons.

CENTIGRADE (C.).—Temperature scale in which freezing point of water is called 0° and boiling point 100°.

CHEMILUMINESCENCE.—Emission of light during a chemical reaction.

COLLOID.—A phase dispersed to such a degree that the surface forces become an important factor in determining its properties.

COMPONENT.—One of the minimum number of substances required to state the composition of all phases of a system.

CONCENTRATION.—The amount of a substance in weight, moles, or equivalents contained in unit volume.

CONDUCTANCE.—Reciprocal of resistance.  $C = \bar{C} A/L$ , where  $A$  is cross section,  $L$ , length, and  $\bar{C}$ , *specific conductance*.

COORDINATION NUMBER OF AN ATOM.—The number of atoms, molecules, or radicals which are held about a central atom in relatively stable positions.

COULOMB.—The quantity of electricity transferred in one second by a current of one ampere; a coulomb can deposit 0.0011180 g. of silver.



- COVALENT BOND.—The term frequently applied to an electron pair bond.
- CRITICAL PRESSURE.—The pressure exerted by a system at its critical temperature.
- CRITICAL TEMPERATURE.—The highest temperature at which a liquid and its vapor may coexist as distinct phases.
- CRITICAL VOLUME.—The volume of unit mass at the critical temperature and pressure.
- CURIE.—The amount of radon which can exist in a steady state, "equilibrium," with 1 g. of radium.
- DECOMPOSITION VOLTAGE.—Cf. Appendix I.
- DEGREE OF FREEDOM.—The number of the variables determining the state of a system (usually pressure, temperature, and concentrations of the components) to which arbitrary values can be assigned.
- DEGREE OF IONIZATION.—Cf. Appendix III.
- DELIQUESCENT.—The term applied to a salt which absorbs moisture from the atmosphere.
- DENSITY (volume-density).—The mass per unit volume: g. per cc.
- DEUTERON.—The nucleus of the deuterium atom.
- DIAMAGNETIC.—An object of diamagnetic material will acquire a magnetic moment opposite to the magnetic field. When a diamagnetic substance is placed in a magnetic field, the lines of force are spread out. (See Paramagnetic.)
- DIELECTRIC CONSTANT.—The force between two point charges ( $e$ ,  $\acute{e}$ ) separated by the distance  $r$  in a uniform medium is  $f = e\acute{e}/kr^2$  where  $k$  is called the dielectric constant.
- DIFFUSION LAW.—The rates of diffusion of two gases are inversely proportional to the square roots of the densities of the gases.
- DISTRIBUTION LAW.—A substance distributes itself between two immiscible solvents so that the ratio of its concentrations in the two solvents is approximately a constant (and equal to the ratio of the solubilities of the substance in each solvent). Requires modification if more than one molecular species is formed.
- DYNE.—Unit of force. The force which will impart to a mass of 1 g. an acceleration of 1 cm. per sec.<sup>2</sup>; 1 g. = 980 dynes.
- ELECTROMOTIVE FORCE.—See Potential.
- ELECTRON.—The unit charge or atom of negative electricity;  $4.774 \times 10^{-10}$  electrostatic units.

- ELECTRON AFFINITY.**—The energy of attachment of an additional electron to a neutral atom.
- ELECTROPOSITIVE ELEMENT.**—An element that is readily oxidized, i.e., forms compounds of positive valence number, syn—base element.
- ELEMENT.**—A substance composed entirely of atoms of the same atomic number.
- ENANTIOTROPIC.**—Crystal forms capable of existing in reversible equilibrium with each other.
- ENERGY.**—Work, or the capacity for doing work.
- ENTROPY.**—A measure of the irreversibility of a process; multiplied by the absolute temperature it is the energy required to restore a system which has changed from state *A* to *B* to its original state. The property is extensive; for all pure crystals it is zero at the absolute zero.
- EQUILIBRIUM, CHEMICAL.**—A state of affairs in which a chemical reaction and its reverse reaction are taking place at equal velocities, so that the concentrations of reacting substances remain constant.
- EQUIVALENT** (g. equivalent weight).—(1) Acid or base: the amount (weight) of substance necessary to give one mole of hydrogen or hydroxyl, respectively, in a neutralization reaction; (2) oxidizing or reducing agent; a mole of substance divided by the number of electrons in the half reaction for the reduction of oxidation considered.
- EQUILIBRIUM CONSTANT.**—The product of the concentrations (or activities) of the substances produced at equilibrium in a chemical reaction divided by the product of concentrations of the reacting substances, each concentration raised to that power which is the coefficient of the substance in the chemical equation.
- ERG.**—Work done by a force of 1 dyne acting through a distance of one cm.
- EUTECTIC.**—The term applied to a minimum in the freezing point-composition curve of a system.
- FAHRENHEIT.**—Temperature scale in which 32° denotes the freezing point and 212° the boiling point of water.
- FARAD.**—Capacity of a condenser which is charged to a potential of 1 volt by 1 coulomb.
- FARADAY.**—96,500 coulombs; the charge of 1 mole ( $6.06 \times 10^{23}$ ) of electrons; the amount of electricity required to precipitate one mole of a singly charged ion.

**FLUORESCENCE.**—The emission of light (other than reflected light) by a substance under illumination.

**FLUX.**—In metallurgy, a substance which will unite with some of the reaction products to form an easily fusible magma.

**FORCE.**—That which is capable of imparting acceleration to a mass.

**FREE ENERGY.**—Cf. Appendix III.

**GAMMA-RAY.**—A very high frequency light wave originating in the nucleus of an atom.

**GAS.**—A state of matter in which a given mass of a substance has neither definite size nor shape.

**GAS CONSTANT.**—The constant of the ideal gas equation relating volume, pressure, temperature, and mass (number of moles).  
 $PV = NRT$ .  $R = 8.315 \times 10^7$  ergs per degree per mole; 0.08206 liter atmos. per degree per mole; 1.9869 cal. (15°) per degree per mole.

**GRAM.**—A unit of mass (or weight). The mass (approximately) of 1 cc. of water at 4° C.

**GRAM ATOM.**—A mass in grams numerically equal to the atomic weight.

**GRAM MOLECULE.**—See Mole. A mass in grams numerically equal to the molecular weight of the substance in question.

**HEAT.**—A form of energy.

**HUMIDITY.**—The amount of water vapor per unit volume of gas. *Relative humidity* is the ratio of the actual partial pressure of water vapor to the equilibrium pressure, water (liquid) to water vapor, at the same temperature.

**HYDRATED OXIDE.**—An oxide which precipitates as a definite compound with water.

**HYDROLYSIS.**—A reaction involving the splitting of water into its ions, and the formation of a weak acid or base or both.

**HYDROUS OXIDE.**—An oxide which precipitates with an indefinite amount of adsorbed water.

**ION.**—A charged atom or chemical radical.

**IONIZATION POTENTIAL.**—The potential required to transfer an electron from its normal quantum level to infinity.

**ISOMERISM.**—Existence of molecules having the same number and kinds of atoms but in different configurations.

**ISOTOPES.**—The term applied to atomic species having the same atomic number but different nuclear structure, as indicated by different atomic weight or different type of radioactivity.

- JOULE.**—Unit of energy =  $10^7$  ergs; work done per second in forcing 1 ampere through a resistance of 1 ohm.
- JOULE-THOMSON EFFECT.**—The temperature change in a gas when it expands without doing external work.
- KELVIN.**—Name applied to absolute-centigrade or thermodynamic temperature scale.
- KERNEL.**—The atomic nucleus plus all of the electrons except those in the valence shell.
- KILO.**—Prefix denoting 1000.
- LATENT HEAT.**—The heat absorbed or evolved in an isothermal reversible process such as melting or vaporization.
- LATTICE ENERGY.**—The energy required to separate the ions of a crystal to an infinite distance from each other.
- LITER.**—A unit of volume, 1000 cc.
- LOSCHMIDT'S NUMBER.**—Equivalent to Avogadro's number.
- MASS.**—Quantity of matter. Determined as the resistance offered by an object to a change of its motion, i.e., inertia.
- MASS LAW.**—See Equilibrium Constant.
- MEGA.**—Prefix meaning 1,000,000.
- MELTING POINT.**—The temperature at which a solid is in equilibrium with its liquid form (varies with pressure).
- METAL.**—A substance possessing so-called metallic properties, i.e., electric conductivity, heat conductivity, high reflectivity, luster, etc., properties due to the high degree of freedom possessed by electrons of the substance.
- MHO.**—One reciprocal ohm.
- MICRO.**—Prefix denoting  $10^{-6}$ .
- MICRON.**—( $\mu$ ) Unit of length =  $10^{-6}$  meters =  $10^{-3}$  mm.
- MILLI.**—Prefix denoting  $10^{-3}$ .
- MOLE.**—The weight of a substance in grams, numerically equal to its molecular weight; a "gram-molecule."
- MOLECULAR VOLUME.**—Volume occupied by one mole. 22.4115 l. at  $0^\circ$  C. and 1 atm.
- MOLECULAR WEIGHT.**—The sum of the atomic weights of all the atoms of the molecule.
- MOLECULE.**—The smallest physical unit of a substance.
- MOMENT OF FORCE.**—The moment about a point = force  $\times$  perpendicular distance from point to line of force.
- MOMENT OF INERTIA.**—The sum of the products of each element of mass times the square of its distance from its axis of rotation.
- MOMENTUM.**—The product of mass times velocity.

**MONOTROPIC.**—Crystal forms one of which is always metastable with respect to the other.

**NEUTRINO.**—The particle whose existence is postulated to account for the apparent non-conservation of energy in  $\beta$ -radiation.

**NEUTRON.**—The elementary particles of atomic weight 1.009 and zero charge.

**NORMAL SOLUTION.**—One having a concentration of 1 equivalent per liter.

**NUCLEUS.**—The positively charged center of the atom. The atom minus the orbital electrons.

**OCTET.**—The term applied to a group of eight electrons in the outer atomic shell.

**OHM.**—Unit of electrical resistance. The resistance of a uniform column of mercury at 0° C. which has a mass of 14.4521 g. and a length of 106.300 cm.

**OHM-CENTIMETER.**—Unit of volume resistivity. A resistance of one ohm across a centimeter cube.

**OVERVOLTAGE.**—Cf. Appendix I.

**OXIDATION.**—An increase in the oxidation state number of an element; the loss of electrons by an atom or group of atoms.

**OXIDATION STATE or NUMBER.**—The charge on a simple ion or for a complex ion or molecule: the charge which is assumed on an atom to account for the number of electrons involved in the oxidation (or reduction) of the atom to the free element.

**PARAMAGNETIC.**—An object of paramagnetic material will acquire a magnetic moment parallel to the magnetic field, and the lines of magnetic force will converge toward it.

**PASSIVE.**—The term applied to the condition produced by treating certain metals with powerful oxidizing agents whereby the metal is rendered in effect more electronegative, e.g., iron treated with fuming nitric acid is rendered passive, and in this condition is not oxidized by silver nitrate solution as is non-passive iron.

**PHASE.**—All of the homogeneous regions of a system which are of the same kind.

**PHASE RULE.**—In a system at equilibrium, the number of phases plus the number of degrees of freedom equals the number of components plus two.

**PHOSPHORESCENCE.**—Remission of light after previous illumination.

PHOTOELECTRIC EFFECT.—The emission of electrons under the action of light.

PHOTON.—A "particle" of radiant energy. ( $E = h\nu$ ).

PLANCK'S CONSTANT.—The constant relating the energy and frequency of radiation.  $E = h\nu$ ,  $h = 6.554 \times 10^{-27}$  erg. sec.

POLARIZATION (electrical).—Refers to a distribution of electrical charges that gives rise to an external electric field.

POLARIZATION (light).—Light is said to be polarized which exhibits different properties in different directions at right angles to the line of propagation.

POLYMORPHISM.—The ability to exist in two or more crystalline forms.

POSITRON.—The positive counterpart of the negative electron.

POTENTIAL (electric, gravitational, etc., at a point in a field).—The work required to move a unit quantity (electron, gram, etc.) from the standard position, or position of reference, to the point in question.

POWER.—The timerate of doing work, e.g., ergs per second.

PRESSURE.—Normal force per unit area.

PROTON.—The unit charge or atom of positive electricity; the nucleus of the hydrogen isotope of mass number one.

QUANTUM NUMBER.—One of the integers defining the energy of an atom.

RADIOACTIVITY.—Changes involving the partial disintegration of the atomic nucleus. Cf. Chapter XXII.

REDUCTION.—The opposite of oxidation; decrease in positive oxidation number; gain in number of electrons by an atom or group of atoms.

REFRACTIVE INDEX.—The ratio of the sine of the angle of incidence of a beam of light from a vacuum upon a substance to the sine of the angle of refraction.  $n = \sin i / \sin r$ . It is also the ratio of velocity of light in vacuum to that in the medium.

REPLACEMENT SERIES.—The arrangement of the metals in order of the values of their oxidation potentials.

RESISTANCE (electrical)  $R$ .—Defined as the quotient of the potential  $E$ , between two surfaces, divided by the resulting current  $I$ , flowing from one to the other, as defined by Ohm's law,  $R = E/I$ .

RYDBERG'S CONSTANT.—A fundamental constant appearing in the expression relating the terms of the hydrogen spectrum.

SOLUBILITY.—The amount of solute (expressed in grams, moles,



etc.) present in a given amount (grams, moles, volume, etc.) of solvent or of solution.

**SOLUBILITY PRODUCT.**—The equilibrium constant for the solution of a solid strong electrolyte, e.g. for  $\text{Cu}_2\text{S}$ ,  $K = (\text{Cu}^+)^2 \times (\text{S}^{--})$ .

**SOLUTE.**—That constituent of a solution which is considered to be dissolved in the other, the solvent. The solvent is usually present in larger amount than the solute.

**SOLUTION.**—A homogeneous mixture, the proportion of whose constituents may be varied within certain limits. Solutions may be either liquid, solid, or gaseous.

**SOLVENT.**—That constituent of a solution which is present in larger amount; or, the constituent which is liquid in the pure state, in the case of solutions of solids or gases in liquids.

**SPECIFIC GRAVITY.**—The ratio of the mass of a certain volume of a substance to the mass of the same volume of a reference substance, generally water, for solids and liquids, and air for gases. The reference substance is at a specified temperature.

**SPECIFIC HEAT.**—The heat required to raise a unit mass (1 g.) of a substance 1 degree.

**SPECIFIC VOLUME.**—The volume of 1 gram of a substance.

**SPECTRUM.**—Light resolved into its component frequencies, as by a prism or diffraction grating.

**STANDARD CONDITIONS** (of a gas).— $0^\circ \text{C}$ . and one atmosphere, or 760 mm. pressure.

**STANDARD POTENTIAL.**—Cf. Appendix I.

**STEPHAN'S CONSTANT.**—The constant relating total black body radiation and the absolute temperature.  $J = \sigma T^4$ .  $\sigma = 5.709 \times 10^{-5}$  erg per  $\text{cm}^2$  per sec. per  $\text{deg}^4$ .

**STOICHIOMETRIC.**—Pertaining to weight relations in chemical reactions.

**SURFACE TENSION.**—The contractive force of a surface measured along unit length of its edge, usually expressed in dynes per  $\text{cm}.$ ; this is numerically equal to the work done in extending the surface 1  $\text{cm}^2$ , in ergs per  $\text{cm}^2$ .

**SYSTEM.**—An isolated group of substances.

**TEMPERATURE.**—The condition which determines whether heat will flow to or from one body to another. See also Absolute, Centigrade.

**THERMOELECTRIC FORCE.**—The potential between the junctions of two metal wires which arises when the two junctions are at different temperatures.

**TRIPLE POINT** (in one component system).—Temperature and pressure at which three phases are in equilibrium, usually refers to liquid-solid-gas systems.

**VALENCE**.—The number of electron pair bonds which an atom shares with other atoms. In inorganic chemistry the term is often used to mean oxidation state (cf. above).

**VAN DER WAALS' EQUATION**.—An equation relating the volume, pressure, and temperature of an imperfect gas in terms of two empirical constants.  $(P + a/v^2)(v - b) = RT$ .

**VISCOSITY**.—The internal friction of a fluid; the reciprocal of fluidity.

**VOLT**.—The potential difference required to produce a current of one ampere through a resistance of one ohm.

**WATT**.—Unit of power, work performed at the rate of one joule per second.

**WAVE LENGTH** (of light).—Distance between consecutive corresponding points in the light wave. Expressed in units of length, Ångstrom, microns, etc. Sodium yellow line =  $5890 \text{ Å} = 589 \times 10^{-6} \text{ mm.} = 0.589 \mu$ .

**X-RAYS**.—High frequency light waves originating from the electrons of the kernel.

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# Appendix I

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## SUMMARY OF FUNDAMENTAL CONCEPTS RELATING TO ELECTROLYTIC OXIDATION AND REDUCTION

(1) An electric current is carried through a solution of an electrolyte by the motion of its ions; the positive ions moving toward the cathode and the negative ions toward the anode. The current carried by each species of ion is proportional to its concentration and velocity.

(2) Electricity is transferred from the electrolyte to the electrodes through the mechanism of electrode reactions, also called "half reactions," which always involve the liberation of electrons at the anode and the using up of electrons at the cathode. The substances entering into either electrode reaction may be positive ions, negative ions, or neutral molecules.

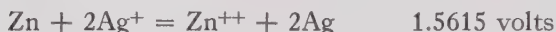
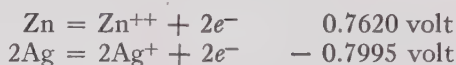
(3) The sum of the two electrode reactions is the cell reaction. If this reaction takes place spontaneously, we have a **battery** or **electric cell** capable of doing external work. If this reaction is not spontaneous, an external electromotive force must be used to force electricity through the cell and the process is called **electrolysis**.

(4) **Faraday Laws.**—The extent of the electrode reactions is proportional to the total current that passes, and the passage of one Faraday (96,500 coulombs) of electricity causes the electrode reaction to proceed to such an extent that one equivalent of each substance involved in the cell reaction is used up or produced.

(5) At the cathode that reduction process occurs which has the highest oxidation potential; and at the anode that oxidation process occurs which has the highest reduction potential, with the exception that the speed of a given electrode reaction may be so slow that a reaction requiring a larger amount of free energy may

take place first. Use may be made of a table of oxidation-reduction potentials, Appendix II, in order to predict the reaction that should theoretically take place at each electrode.

The potential of the cell reaction is the difference in potential of the two half reactions, e.g.,



(6) The standard potential values are based upon measurements with very small currents. In general, if a solution is being electrolyzed with appreciable current, the potential required is greater than the reversible electrode potentials, due to irreversible changes taking place.

$$E_{\text{electrolysis}} = E_{0(\text{reversible})} + E_{\text{irreversible}}$$

The irreversible potential required is known as **overvoltage** and may be traced to three general causes:

**First.** The potential necessary to overcome the resistance of the solution.

**Second.** If a large current is flowing, the resistance of the electrolyte may increase very markedly, due to the rapidity with which the ions are being used up in the immediate vicinity of the

TABLE I  
OVERVOLTAGES, IN VOLTS, OF HYDROGEN, OXYGEN, AND CHLORINE  
AT 25° C.

CURRENT DENSITIES IN AMPERES PER CM.<sup>2</sup>

NATURE OF ELECTRODE	H <sub>2</sub> IN 1 M H <sub>2</sub> SO <sub>4</sub>				H <sub>2</sub> IN 1 M NaOH	O <sub>2</sub> IN 1 M NaOH			O <sub>2</sub> IN 1 M H <sub>2</sub> SO <sub>4</sub>	Cl <sub>2</sub> IN NaCl
	Current Density				Current Density 0.01	Current Density			Current Density 0.1	Current Density 0.01 0.1
	0.001	0.01	0.1	1.0		0.01	0.1	1.0		
Pt (smooth)		0.07	0.28	0.68	0.54	0.85	1.28	1.49		
Pt (black)	0.003	0.03	0.04	0.05		0.52	0.64	0.77		0.03 0.05
Au	0.12	0.39	0.59	0.80		0.96	1.24	1.63		0.02 0.03
Cu	0.35	0.58	0.80	1.25	0.91	0.58	0.66	0.79		
Ag	0.30	0.76	0.87	1.08	0.61	0.73	0.98	1.13		
Al	0.50	0.83	1.00	1.29						
Sn	0.40	1.08	1.22	1.23	0.94					
Zn		0.75	1.06	1.23	1.05					
Pb		1.09	1.18	1.26						
Fe	0.22	0.56	0.81	1.29	0.54	0.55				
Hg	0.6	1.04	1.06	1.12						
C (graphite)	0.31	0.78	0.98	1.22		0.90	1.09	1.24		0.25

electrodes. This effect is sometimes known as **concentration polarization**.

**Third.** Many of the electrode reactions are slow, and in order to get them to go with the speed required by large currents, additional potential or driving force must be used. This is especially true of gas reactions. These overvoltages depend not only upon the current density but also upon the nature of the electrode, as is indicated by the experimental results given in Table I. Overvoltage decreases with increasing temperature.

TABLE II  
OVERVOLTAGES OF METAL IONS, VOLTS

ELECTRODE	CURRENT DENSITY, I/cm. <sup>2</sup>		
	0.0001	0.002	0.1
Fe in Fe <sup>++</sup>	0.129	0.141	0.3
Cu in Cu <sup>++</sup>	0.011	0.013	0.02
Ag in Ag <sup>+</sup>			0.00
Zn in Zn <sup>++</sup>			0.02
Ni in Ni <sup>++</sup>			0.8

# Appendix II

## STANDARD OXIDATION-REDUCTION POTENTIALS

VALUES, IN VOLTS, REFERRED TO THE HYDROGEN-HYDROGEN ION COUPLE AS ZERO, ARE FOR UNIT ACTIVITIES AND TEMPERATURE OF 25° C.

(Cf. notes at end of table)

*Acid Solutions*

COUPLE	$E^\circ$	COUPLE	$E^\circ$
$\text{Li} = \text{Li}^+ + e^-$	3.02	$\text{Cl}^- + \text{Ti} = \text{TiCl} + e^-$	0.557
$\text{Cs} = \text{Cs}^+ + e^-$	3.02	$\text{AsH}_3 = \text{As} + 3\text{H}^+ + 3e^-$	0.54
$\text{Rb} = \text{Rb}^+ + e^-$	2.99	$\text{Ga} = \text{Ga}^{+++} + 3e^-$	0.52
$\text{K} = \text{K}^+ + e^-$	2.922	$\text{H}_2\text{C}_2\text{O}_4(\text{aq}) = 2\text{CO}_2(\text{g}) + 2\text{H}^+ + 2e^-$	0.49
$\text{Ba} = \text{Ba}^{++} + 2e^-$	2.90	$\text{Fe} = \text{Fe}^{++} + 2e^-$	0.440
$\text{Sr} = \text{Sr}^{++} + 2e^-$	2.89	$\text{H}_2 = 2\text{H}^+(10^{-7}M) + 2e^-$	0.414
$\text{Ca} = \text{Ca}^{++} + 2e^-$	2.87	$\text{Cr}^{++} = \text{Cr}^{+++} + e^-$	0.41
$\text{Na} = \text{Na}^+ + e^-$	2.712	$\text{Cd} = \text{Cd}^{++} + 2e^-$	0.4020
$\text{La} = \text{La}^{+++} + 3e^-$	2.37	$\text{SO}_4^{--} + \text{Pb} = \text{PbSO}_4 + 2e^-$	0.355
$\text{Mg} = \text{Mg}^{++} + 2e^-$	2.34	$\text{Tl} = \text{Tl}^+ + e^-$	0.3363
$\text{H}^- = \frac{1}{2}\text{H}_2 + e^-$	2.33	$2\text{H}_2\text{O} + \text{P} = \text{H}_3\text{PO}_2 + \text{H}^+ + e^-$	0.29
$\text{Ti} = \text{Ti}^{++} + 2e^-$	1.75	$\text{Co} = \text{Co}^{++} + 2e^-$	0.277
$\text{Be} = \text{Be}^{++} + 2e^-$	1.70	$2\text{Cl}^- + \text{Pb} = \text{PbCl}_2 + 2e^-$	0.268
$\text{Al} = \text{Al}^{+++} + 3e^-$	1.67	$\text{Ni} = \text{Ni}^{++} + 2e^-$	0.250
$\text{Mn} = \text{Mn}^{++} + 2e^-$	1.05	$\text{V}^{++} = \text{V}^{+++} + e^-$	0.20
$2\text{H}_2\text{O} + \text{Si} = \text{SiO}_2 + 4\text{H}^+ + 4e^-$	0.84	$\text{H}_2\text{O} + \text{H}_3\text{PO}_3 = \text{H}_3\text{PO}_4 + 2\text{H}^+ + 2e^-$	0.20
$\text{Zn} = \text{Zn}^{++} + 2e^-$	0.7620	$\text{I}^- + \text{Cu} = \text{CuI} + e^-$	0.187
$3\text{H}_2\text{O} + \text{B} = \text{H}_3\text{BO}_3 + 3\text{H}^+ + 3e^-$	0.73	$\text{I}^- + \text{Ag} = \text{AgI} + e^-$	0.151
$5\text{H}_2\text{O} + 2\text{Ta} = \text{Ta}_2\text{O}_5 + 10\text{H}^+ + 10e^-$	0.71	$\text{HCOOH}(\text{aq}) = \text{CO}_2(\text{g}) + 2\text{H}^+ + 2e^-$	0.14
$\text{Cr} = \text{Cr}^{+++} + 3e^-$	0.71	$\text{Sn} = \text{Sn}^{++} + 2e^-$	0.136
$\text{H}_2\text{Te}(\text{aq}) = \text{Te} + 2\text{H}^+ + 2e^-$	0.69		
$\text{H}_2\text{O} + \text{H}_3\text{PO}_2 = \text{H}_3\text{PO}_3 + 2\text{H}^+ + 2e^-$	0.59		



## Acid Solutions (Cont'd)

COUPLE	$E^\circ$	COUPLE	$E^\circ$
$\text{Pb} = \text{Pb}^{++} + 2e^-$	0.126	$\text{Fe}(\text{CN})_6^{-4} = \text{Fe} - (\text{CN})_6^{---} + e^-$	- 0.36
$2\text{I}^- + 2\text{Hg} = \text{Hg}_2\text{I}_2 + 2e^-$	0.0405	$3\text{H}_2\text{O} + \text{S}_2\text{O}_3^{--} = 2\text{H}_2\text{SO}_3 + 2\text{H}^+ + 4e^-$	- 0.40
$4\text{I}^- + \text{Hg} = \text{HgI}_4^- + 2e^-$	0.04	$3\text{H}_2\text{O} + \text{S} = \text{H}_2\text{SO}_3 + 4\text{H}^+ + 4e^-$	- 0.45
$\text{PH}_3(\text{g}) = \text{P} + 3\text{H}^+ + 3e^-$	0.04	$\text{I}^- + \text{Au} = \text{AuI} + e^-$	- 0.50
$\text{Fe} = \text{Fe}^{+++} + 3e^-$	0.036	$\text{Cu} = \text{Cu}^+ + e^-$	- 0.522
$\text{H}_2 = 2\text{H}^+ + 2e^-$	0.000	$2\text{H}_2\text{O} + \text{Te} = \text{TeO}_2(\text{s}) + 4\text{H}^+ + 4e^-$	- 0.529
$2\text{S}_2\text{O}_3^{--} + \text{Ag} = \text{Ag} - (\text{S}_2\text{O}_3)_2^{---} + e^-$	- 0.01	$2\text{I}^- = \text{I}_2 + 2e^-$	- 0.5345
$\text{Br}^- + \text{Cu} = \text{CuBr} + e^-$	- 0.033	$3\text{I}^- = \text{I}_3^- + 2e^-$	- 0.5355
$\text{Br}^- + \text{Ag} = \text{AgBr} + e^-$	- 0.073	$2\text{H}_2\text{O} + \text{HAsO}_2 = \text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2e^-$	- 0.559
$\text{H}_2\text{O} + \text{Ti}^{+++} = \text{TiO}^{++} + 2\text{H}^+ + e^-$	ca - 0.1	$2\text{H}_2\text{O} + \text{Te} = \text{TeO}_2\text{H}^+ + 3\text{H}^+ + 4e^-$	- 0.559
$\text{Cl}^- + \text{Cu} = \text{CuCl} + e^-$	- 0.124	$\text{CuCl} = \text{Cu}^{++} + \text{Cl}^- + e^-$	- 0.566
$2\text{Br}^- + 2\text{Hg} = \text{Hg}_2\text{Br}_2 + 2e^-$	- 0.1397	$\text{SO}_4^{--} + 2\text{Hg} = \text{Hg}_2\text{SO}_4 + 2e^-$	- 0.6151
$\text{H}_2\text{S} = \text{S} + 2\text{H}^+ + 2e^-$	- 0.141	$2\text{Br}^- + \text{PtBr}_4^{--} = \text{PtBr}_6^{--} + 2e^-$	- 0.63
$4\text{H}_2\text{O} + \text{Re} = \text{ReO}_4^- + 8\text{H}^+ + 7e^-$	- 0.15	$4\text{Cl}^- + \text{Pd} = \text{PdCl}_4^{--} + 2e^-$	- 0.64
$\text{Sn}^{++} = \text{Sn}^{+4} + 2e^-$	- 0.15	$3\text{H}_2\text{O} + 2\text{SbO}^+ = \text{Sb}_2\text{O}_5 + 6\text{H}^+ + 4e^-$	- 0.64
$4\text{Cl}^- + \text{Bi} = \text{BiCl}_4^- + 3e^-$	- 0.16	$\text{SO}_4^{--} + 2\text{Ag} = \text{Ag}_2\text{SO}_4 + 2e^-$	- 0.653
$\text{Cu}^+ = \text{Cu}^{++} + e^-$	- 0.167	$\text{CuBr} = \text{Cu}^{++} + \text{Br}^- + e^-$	- 0.657
$2\text{Cl}^- + \text{Cu} = \text{CuCl}_2^- + e^-$	- 0.19	$2\text{H}_2\text{O} + 2\text{SbO}^+ = \text{Sb}_2\text{O}_4 + 4\text{H}^+ + 2e^-$	- 0.68
$\text{H}_2\text{O} + \text{H}_2\text{SO}_3 = \text{SO}_4^{--} + 4\text{H}^+ + 2e^-$	- 0.20	$\text{H}_2\text{O}_2 = \text{O}_2 + 2\text{H}^+ + 2e^-$	- 0.682
$4\text{Br}^- + \text{Hg} = \text{HgBr}_4^{--} + 2e^-$	- 0.21	$2\text{Cl}^- + \text{PtCl}_4^{--} = \text{PtCl}_6^{--} + 2e^-$	- 0.72
$\text{Sb} + \text{H}_2\text{O} = \text{SbO}^+ + 2\text{H}^+ + 3e^-$	- 0.212	$6\text{Cl}^- + \text{Ir} = \text{IrCl}_6^{---} + 3e^-$	- 0.72
$\text{Cl}^- + \text{Ag} = \text{AgCl} + e^-$	- 0.2222	$4\text{Cl}^- + \text{Pt} = \text{PtCl}_4^{--} + 2e^-$	- 0.73
$2\text{H}_2\text{O} + \text{As} = \text{HAsO}_2 - (\text{aq}) + 3\text{H}^+ + 3e^-$	- 0.2475	$\text{Se} + 3\text{H}_2\text{O} = \text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4e^-$	- 0.740
$2\text{Cl}^- + 2\text{Hg} = \text{Hg}_2\text{Cl}_2 + 2e^-$	- 0.2676	$2\text{CNS}^- = (\text{CNS})_2 + 2e^-$	- 0.77
$\text{H}_2\text{O} + \text{V}^{+++} = \text{VO}^{++} + 2\text{H}^+ + e^-$	- 0.314	$\text{Fe}^{++} = \text{Fe}^{+++} + e^-$	- 0.771
$\text{H}_2\text{O} + \text{Bi} = \text{BiO}^+ + 2\text{H}^+ + 3e^-$	- 0.32		
$\text{UO}_2 = \text{UO}_2^{++} + 2e^-$	- 0.33		
$\text{HCN} = \frac{1}{2}\text{C}_2\text{N}_2(\text{g}) + \text{H}^+ + e^-$	- 0.33		
$\text{Cu} = \text{Cu}^{++} + 2e^-$	- 0.3448		

## Acid Solutions (Cont'd)

COUPLE	$E^\circ$	COUPLE	$E^\circ$
$2\text{Hg} = \text{Hg}_2^{++} + 2e^-$	- 0.7986	$\text{TiCl} = \text{Ti}^{+++} + \text{Cl}^-$	
$\text{Ag} = \text{Ag}^+ + e^-$	- 0.7995	$+ 2e^-$	- 1.36
$2\text{H}_2\text{O} + \text{N}_2\text{O}_4 = 2\text{NO}_3^-$		$7\text{H}_2\text{O} + 2\text{Cr}^{+++}$	
$+ 4\text{H}^+ + 2e^-$	- 0.81	$= \text{Cr}_2\text{O}_7^{--} + 14\text{H}^+$	
$2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+$		$+ 6e^-$	- 1.36
$(10^{-7}M) + 4e^-$	- 0.815	$3\text{H}_2\text{O} + 2\text{Au} = \text{Au}_2\text{O}_3$	
$2\text{Br}^- + \text{AuBr}_2^-$		$+ 6\text{H}^+ + 6e^-$	- 1.363
$= \text{AuBr}_4^- + 2e^-$	- 0.82	$\text{Au} = \text{Au}^{+++} + 3e^-$	- 1.42
$\text{Pd} = \text{Pd}^{++} + 2e^-$	- 0.83	$3\text{H}_2\text{O} + \text{Br}^- = \text{BrO}_3^-$	
$\text{Hg} = \text{Hg}^{++} + 2e^-$	- 0.854	$+ 6\text{H}^+ + 6e^-$	- 1.44
$\text{Hg}_2^{++} = 2\text{Hg}^{++} + 2e^-$	- 0.910	$3\text{H}_2\text{O} + \text{Cl}^- = \text{ClO}_3^-$	
$2\text{H}_2\text{O} + \text{NO} = \text{NO}_3^-$		$+ 6\text{H}^+ + 6e^-$	- 1.45
$+ 4\text{H}^+ + 3e^-$	- 0.96	$2\text{H}_2\text{O} + \text{Pb}^{++} = \text{PbO}_2$	
$2\text{Br}^- + \text{Au} = \text{AuBr}_2^-$		$+ 4\text{H}^+ + 2e^-$	- 1.456
$+ e^-$	- 0.96	$\frac{1}{2}\text{Cl}_2 + 3\text{H}_2\text{O} = 6\text{H}^+$	
$\text{NO} + \text{H}_2\text{O} = \text{HNO}_2$		$+ \text{ClO}_3^- + 5e^-$	- 1.47
$+ \text{H}^+ + e^-$	- 0.99	$\text{Mn}^{++} = \text{Mn}^{+++} + e^-$	- 1.51
$3\text{H}_2\text{O} + \text{VO}^{++} = \text{V}(\text{OH})_4^+ + 2\text{H}^+ + e^-$	- 1.000	$\frac{1}{2}\text{Br}_2 + 3\text{H}_2\text{O} = \text{BrO}_3^-$	
$4\text{Cl}^- + \text{Au} = \text{AuCl}_4^-$		$+ 6\text{H}^+ + 5e^-$	- 1.52
$+ 3e^-$	- 1.00	$4\text{H}_2\text{O} + \text{Mn}^{++}$	
$\text{ClO}_3^- + \text{H}_2\text{O} = 2\text{H}^+$		$= \text{MnO}_4^- + 8\text{H}^+$	
$+ \text{ClO}_4^- + 2e^-$	- 1.00	$+ 5e^-$	- 1.52
$4\text{H}_2\text{O} + \text{TeO}_2(\text{s})$		$2\text{H}_2\text{O} + 2\text{BiO}^+ = \text{Bi}_2\text{O}_4$	
$= \text{H}_6\text{TeO}_6(\text{s}) + 2\text{H}^+$		$+ 4\text{H}^+ + 2e^-$	ca - 1.59
$+ 2e^-$	- 1.02	$\frac{1}{2}\text{Br}_2 + \text{H}_2\text{O} = \text{HBrO}$	
$2\text{Br}^- = \text{Br}_2(1) + 2e^-$	- 1.0652	$+ \text{H}^+ + e^-$	- 1.59
$3\text{H}_2\text{O} + \text{I}^- = \text{IO}_3^-$		$\text{Ce}^{+3} = \text{Ce}^{+4} + e^-$	- 1.61
$+ 6\text{H}^+ + 6e^-$	- 1.085	$\frac{1}{2}\text{Cl}_2 + \text{H}_2\text{O} = \text{H}^+$	
$2\text{Br}^- = \text{Br}_2(\text{aq}) + 2e^-$	- 1.087	$+ \text{HClO} + e^-$	- 1.63
$\text{H}_2\text{O} + \text{H}_2\text{SeO}_3$		$\frac{1}{2}\text{Cl}_2 + 2\text{H}_2\text{O} = 3\text{H}^+$	
$= \text{SeO}_4^{--} + 4\text{H}^+ + 2e^-$	- 1.15	$+ \text{HClO}_2 + 3e^-$	- 1.63
$\frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O} = \text{IO}_3^-$		$2\text{H}_2\text{O} + \text{MnO}_2$	
$+ 6\text{H}^+ + 5e^-$	- 1.195	$= \text{MnO}_4^- + 4\text{H}^+$	
$\text{Pt} = \text{Pt}^{++} + 2e^-$	ca - 1.2	$+ 3e^-$	- 1.67
$2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+$		$\text{Au} = \text{Au}^+ + e^-$	- 1.68
$+ 4e^-$	- 1.229	$2\text{H}_2\text{O} + \text{PbSO}_4 = \text{PbO}_2$	
$\text{Ti}^+ = \text{Ti}^{+++} + 2e^-$	- 1.25	$+ \text{SO}_4^{--} + 4\text{H}^+ + 2e^-$	- 1.685
$2\text{H}_2\text{O} + \text{Mn}^{++} = \text{MnO}_2$		$3\text{H}_2\text{O} + \text{IO}_3^- = \text{H}_6\text{IO}_6$	
$+ 4\text{H}^+ + 2e^-$	- 1.28	$+ \text{H}^+ + 2e^-$	ca - 1.7
$\text{PdCl}_4^{--} + 2\text{Cl}^-$		$2\text{H}_2\text{O} + \text{Ni}^{++} = \text{NiO}_2$	
$= \text{PdCl}_2^{--} + 2e^-$	- 1.288	$+ 4\text{H}^+ + 2e^-$	- 1.75
$\text{Au}^+ = \text{Au}^{+++} + 2e^-$	ca - 1.29	$2\text{H}_2\text{O} = \text{H}_2\text{O}_2 + 2\text{H}^+$	
$\frac{1}{2}\text{Cl}_2 + 4\text{H}_2\text{O} = 8\text{H}^+$		$+ 2e^-$	- 1.77
$+ \text{ClO}_4^- + 7e^-$	- 1.34	$\text{Co}^{++} = \text{Co}^{+++} + e^-$	- 1.84
$\text{H}_2\text{O} + \text{NH}_4^+ = \text{NH}_3\text{OH}^+$		$\text{Ag}^+ = \text{Ag}^{++} + e^-$	- 1.98
$+ 2\text{H}^+ + 2e^-$	- 1.35	$2\text{SO}_4^{--} = \text{S}_2\text{O}_8^{--} + 2e^-$	- 2.05
$\text{Cl}^- = \frac{1}{2}\text{Cl}_2 + e^-$	- 1.3583	$\text{O}_2 + \text{H}_2\text{O} = \text{O}_3 + 2\text{H}^+$	
		$+ 2e^-$	- 2.07

*Acid Solutions (Concluded)*

COUPLE	$E^\circ$	COUPLE	$E^\circ$
$\text{H}_2\text{O} + 2\text{F}^- = \text{F}_2\text{O}$ $+ 2\text{H}^+ + 4e^-$	- 2.1	$2\text{F}^- = \text{F}_2 + 2e^-$ $2\text{HF} = \text{F}_2 + 2\text{H}^+ + 2e^-$	- 2.85 - 3.03

*Basic Solutions*

COUPLE	$E^\circ$	COUPLE	$E^\circ$
$2\text{OH}^- + \text{Ca} = \text{Ca(OH)}_2$ $+ 2e^-$	3.02	$\text{H}_2\text{O} + 3\text{OH}^- + \text{HSnO}_2^-$ $= \text{Sn(OH)}_6^{--} + 2e^-$	0.96
$8\text{H}_2\text{O} + 2\text{OH}^- + \text{Sr}$ $= \text{Sr(OH)}_2 \cdot 8\text{H}_2\text{O}$ $+ 2e^-$	2.99	$\text{Te}^{--} = \text{Te} + 2e^-$	0.92
$8\text{H}_2\text{O} + 2\text{OH}^- + \text{Ba}$ $= \text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ $+ 2e^-$	2.97	$2\text{OH}^- + \text{SO}_3^{--} = \text{SO}_4^{--}$ $+ \text{H}_2\text{O} + 2e^-$	0.90
$3\text{OH}^- + \text{La} = \text{La(OH)}_3$ $+ 3e^-$	2.76	$2\text{OH}^- + \text{Fe} = \text{Fe(OH)}_2$ $+ 2e^-$	0.877
$2\text{OH}^- + \text{Mg} = \text{Mg-}$ $(\text{OH})_2 + 2e^-$	2.67	$3\text{OH}^- + \text{PH}_3(\text{g}) = \text{P}$ $+ 3\text{H}_2\text{O} + 3e^-$	0.87
$4\text{OH}^- + \text{Al} = \text{H}_2\text{AlO}_3^-$ $+ \text{H}_2\text{O} + 3e^-$	2.35	$\text{S}^{--} + \text{Ni} = \text{NiS}(\alpha)$ $+ 2e^-$	0.86
$2\text{OH}^- + \text{P} = \text{H}_2\text{PO}_2^-$ $+ e^-$	1.82	$4\text{OH}^- + \text{N}_2\text{O}_4 = 2\text{NO}_3^-$ $+ 2\text{H}_2\text{O} + 2e^-$	0.85
$6\text{OH}^- + \text{Si} = \text{SiO}_3^{--}$ $+ 3\text{H}_2\text{O} + 4e^-$	1.73	$\text{H}_2 + 2\text{OH}^- = 2\text{H}_2\text{O}$ $+ 2e^-$	0.828
$2\text{OH}^- + \text{Mn} = \text{Mn-}$ $(\text{OH})_2 + 2e^-$	1.47	$2\text{OH}^- + \text{Cd} = \text{Cd(OH)}_2$ $+ 2e^-$	0.815
$\text{S}^{--} + \text{Zn} = \text{ZnS} + 2e^-$	1.44	$3\text{OH}^- + \text{Sn} = \text{HSnO}_2^-$ $+ \text{H}_2\text{O} + 2e^-$	0.79
$3\text{OH}^- + \text{Cr} = \text{Cr(OH)}_3$ $+ 3e^-$	1.3	$\text{Se}^{--} = \text{Se} + 2e^-$	0.78
$\text{S}^{--} + \text{Cd} = \text{CdS}$ $+ 2e^-$	1.23	$2\text{OH}^- + \text{Co} = \text{Co(OH)}_2$ $+ 2e^-$	0.73
$4\text{OH}^- + \text{Ga} = \text{H}_2\text{GaO}_3^-$ $+ \text{H}_2\text{O} + 3e^-$	1.22	$4\text{OH}^- + \text{AsO}_2^-$ $= \text{AsO}_4^{--} + 2\text{H}_2\text{O}$ $+ 2e^-$	0.71 0.70
$4\text{OH}^- + \text{Zn} = \text{ZnO}_2^{--}$ $+ 2\text{H}_2\text{O} + 2e^-$	1.216	$\text{S}^{--} + \text{Hg} = \text{HgS} + 2e^-$	
$4\text{OH}^- + \text{Cr} = \text{CrO}_2^-$ $+ 2\text{H}_2\text{O} + 3e^-$	1.2	$4\text{OH}^- + \text{As} = \text{AsO}_2^-$ $+ 2\text{H}_2\text{O} + 3e^-$	0.68
$\text{HCHO}(\text{aq}) + 3\text{OH}^-$ $+ \text{HCO}_2^-(\text{aq})$ $+ 2\text{H}_2\text{O} + 2e^-$	1.114	$4\text{OH}^- + \text{Sb} = \text{SbO}_2^-$ $+ 2\text{H}_2\text{O} + 3e^-$	0.66
$3\text{OH}^- + \text{HPO}_3^{--}$ $= \text{PO}_4^{--} + \text{H}_2\text{O}$ $+ 2e^-$	1.05	$2\text{OH}^- + \text{Ni} = \text{Ni(OH)}_2$ $+ 2e^-$	0.66
$4\text{NH}_3(\text{aq}) + \text{Zn}$ $= \text{Zn(NH}_3)_4^{++} + 2e^-$	1.03	$2\text{CN}^- + \text{Au} = \text{Au-}$ $(\text{CN})_2^- + e^-$	0.60
$\text{S}^{--} + \text{Fe} = \text{FeS} + 2e^-$	1.00	$4\text{NH}_3 + \text{Cd} = \text{Cd-}$ $(\text{NH}_3)_4^{++} + 2e^-$	0.597
$\text{S}^{--} + \text{Pb} = \text{PbS} + 2e^-$	0.98	$2\text{OH}^- + \text{Pb} = \text{PbO}(\text{r})$ $+ \text{H}_2\text{O} + 2e^-$	0.578
		$\text{OH}^- + \text{Fe(OH)}_2$ $= \text{Fe(OH)}_3 + e^-$	0.56
		$2\text{S}^{--} = \text{S}_2^{--} + 2e^-$	0.51

*Basic Solutions (Concluded)*

COUPLE	$E^\circ$	COUPLE	$E^\circ$
$S^{--} = S + 2e^-$	0.508	$2OH^- + ClO_3^- = ClO_4^- + H_2O + 2e^-$	- 0.17
$6NH_3(aq) + Ni = Ni-(NH_3)_6^{++} + 2e^-$	0.48	$OH^- + Co(OH)_2 = Co-(OH)_3 + e^-$	- 0.2
$NO + 2OH^- = NO_2^- + H_2O + e^-$	0.46	$6OH^- + I^- = IO_3^- + 3H_2O + 6e^-$	- 0.26
$3OH^- + Bi = BiOOH + H_2O + 3e^-$	0.46	$2OH^- + 2Ag = Ag_2O + H_2O + 2e^-$	- 0.344
$OH^- + Mn(OH)_2 = Mn(OH)_3 + e^-$	0.40	$4OH^- = O_2 + 2H_2O + 4e^-$	- 0.401
$2OH^- + 2Cu = Cu_2O + H_2O + 2e^-$	0.361	$NH_4OH + 2OH^- = NH_2OH + 2H_2O + 2e^-$	- 0.42
$OH^- + Tl = Tl(OH) + e^-$	0.3445	$2OH^- + Ni(OH)_2 = NiO_2 + 2H_2O + 2e^-$	- 0.49
$2OH^- + Cu = Cu(OH)_2 + 2e^-$	0.224	$MnO_4^{--} = MnO_4^- + e^-$	- 0.54
$5OH^- + Cr(OH)_3 = CrO_4^{--} + 4H_2O + 3e^-$	0.12	$4OH^- + IO^- = IO_3^- + 2H_2O + 4e^-$	- 0.56
$2NH_3 + Cu = Cu-(NH_3)_2^+ + e^-$	0.11	$4OH^- + MnO_2 = MnO_4^- + 2H_2O + 3e^-$	- 0.57
$H_2O + 2OH^- + Cu_2O = 2Cu(OH)_2 + 2e^-$	0.09	$2OH^- + Ag_2O = 2AgO + H_2O + 2e^-$	- 0.57
$OH^- + HO_2^- = O_2 + H_2O + 2e^-$	0.076	$4OH^- + MnO_2 = MnO_4^{--} + 2H_2O + 2e^-$	- 0.58
$4NH_3 + Cu = Cu-(NH_3)_4^{++} + 2e^-$	0.05	$2OH^- + ClO^- = ClO_2^- + H_2O + 2e^-$	- 0.59
$2OH^- + Tl(OH) = Tl-(OH)_3 + 2e^-$	0.05	$6OH^- + Br^- = BrO_3^- + 3H_2O + 6e^-$	- 0.61
$6OH^- + Te = TeO_3^{--} + 2H_2O + 4e^-$	0.02	$6OH^- + Cl^- = ClO_3^- + 3H_2O + 6e^-$	- 0.62
$2OH^- + NO_2^- = NO_3^- + H_2O + 2e^-$	- 0.01	$3OH^- + IO_3^- = H_3IO_6^{--} + 2e^-$	ca - 0.70
$2OH^- + SeO_3^{--} = SeO_4^{--} + H_2O + 2e^-$	- 0.03	$2OH^- + 2AgO = Ag_2O_3 + H_2O + 2e^-$	- 0.74
$Hg + 2OH^- = HgO(r) + H_2O + 2e^-$	- 0.0984	$4OH^- + Cl^- = ClO_2^- + 2H_2O + 4e^-$	- 0.76
$2OH^- + Pd = Pd(OH)_2 + 2e^-$	- 0.1	$2OH^- + Br^- = BrO^- + H_2O + 2e^-$	- 0.76
$6OH^- + 2Ir = Ir_2O_3 + 3H_2O + 6e^-$	- 0.1	$3OH^- = HO_2^- + H_2O + 2e^-$	- 0.87
$2OH^- + 2Hg = Hg_2O + H_2O + 2e^-$	- 0.123	$2NO_2^- = N_2O_4 + 2e^-$	- 0.88
$N_2O + 6OH^- = 2NO_2^- + 3H_2O + 4e^-$	- 0.15	$2OH^- + Cl^- = ClO^- + H_2O + 2e^-$	- 0.94
$2OH^- + Pt = Pt(OH)_2 + 2e^-$	- 0.16	$O_2 + 2OH^- = O_3 + H_2O + 2e^-$	- 1.4

# NOTES ON THE USE OF THE TABLE OF OXIDATION-REDUCTION POTENTIALS

The above table of important oxidation-reduction potentials has been prepared for ready reference. Additional values for couples less frequently employed will be found under the various elements.

The  $E^\circ$  values for couples involving  $1M\ H^+$  have been given in the first part of the table and those for couples involving  $1M\ OH^-$  in the second part. The potential of many couples is independent of pH and although these have been included in the table for acidic reactions, they might have been repeated for the latter table.

The couples are arranged in order of increasing oxidizing power, that is, the oxidized form of any couple has sufficient energy to oxidize the reduced form of any couple of higher positive potential.

The convention regarding the sign of the  $E^\circ$  values is that used throughout the text. The couple is written with the electrons on the right side and the sign is positive if the reduced form of the couple (written on left side) is a better reducing agent than  $H_2$ .

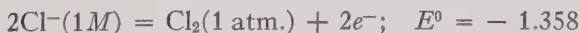
The values, which are referred to the potential of the hydrogen-hydrogen ion couple as zero, are for  $25^\circ\ C.$  and all gas pressures, 1 atmosphere, and all activities (Append. IV), 1 molal, unless otherwise stated.

The potential at other concentrations and pressures at  $25^\circ\ C.$  is given by the expression:

$$E = E^\circ - \frac{0.059}{n} \log Q,$$

where  $Q$  is the product of the activities (solutes in moles per liter and gases in atmospheres) of the products divided by the product of the activities of the reacting substances, each activity raised to that power whose exponent is the coefficient of the substance in the half reaction, and  $n$  is the number of moles of electrons involved in the half reaction as written. Activities of pure solids and liquids are taken as unity.

*Example:*



$$E = -1.358 - 0.138 = -1.496$$

These potential values merely represent the difference in energies of the products and the reacting substances and as such give no information as to the speed of the reaction; indeed the mechanism of the reaction may be such that it cannot take place in spite of a favorable potential value. Thus,  $\text{Fe} = \text{Fe}^{+++} + 3e^-$ ;  $+ 0.04$  volt, indicates that  $\text{H}^+$  would oxidize iron to the ferric state, but the mechanism of the reaction is  $\text{Fe} = \text{Fe}^{++} + 2e^-$ ,

$+ 0.44$  volt, and  $\text{Fe}^{++} = \text{Fe}^{+++} + e^-$ ,  $- 0.77$  volt, and  $\text{H}^+$  cannot bring about the second step.

In general it may be stated that many of the reactions given are not capable of experimental attainment under equilibrium conditions for one of two reasons: (1) the reaction is slow, as, for example, the reduction of sulfuric acid to sulfurous acid in dilute solutions, or the evolution of hydrogen on zinc which may require an overvoltage of 1.2 volts; or (2) the final and initial substances cannot exist together because of an intermediate state, as for example, the  $\text{Fe} - \text{Fe}^{+++}$  couple which gives  $\text{Fe}^{++}$ , or  $\text{Cl}^- + \text{H}_2\text{O} = \text{HClO} + \text{H}^+ + 2e^-$ , which would give  $\text{Cl}_2$  at  $1M \text{H}^+$ .

Two half reactions may be added or subtracted to give a third half reaction but the potential of the third reaction is derived by the *addition or subtraction of the free energies* (Append. III) and not by the addition of the potential values. However, if two half reactions are subtracted to give a complete reaction, the potential of the reaction is the *difference in the potentials of the two couples*.

The change in the half reaction-potentials with change in  $\text{H}^+$  concentration for a number of couples is shown graphically in Fig. 1. The various couples given in the figure are as follows:

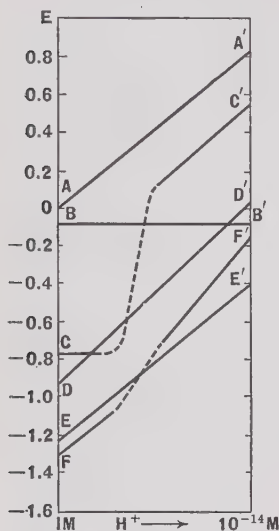
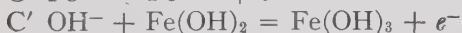
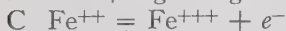
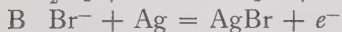
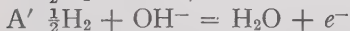
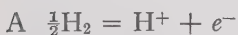
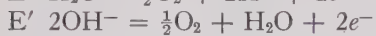
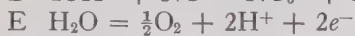


FIG. 1. Change of  $E$  with concentration of  $\text{H}^+$ .





# Appendix III

## FREE ENERGY VALUES AND THEIR USE

Summary of concepts relating to free energy data, and their use in predicting the direction and extent to which a given reaction will proceed:

(1) The free energy of a process is the maximum available work which is obtainable in going from the initial to the final state. The free energy change,  $\Delta F$ , of a chemical reaction is the free energies of formation (from their elements) of the products of the reaction, less the free energy of formation of the reacting substances. *Example:*  $\text{CaO} + 2\text{HCl} = \text{CaCl}_2 + \text{H}_2\text{O}$ ;  $\Delta F = F_{\text{CaCl}_2} + F_{\text{H}_2\text{O}} - F_{\text{CaO}} - 2F_{\text{HCl}}$ .

(2) The free energy values for the substances in Table I refer to energy of formation from the elements at  $25^\circ$  in their standard states or states of unit activity, which are pure solid, pure liquid, gas at one atmosphere, and solute at 1 molal activity. The free energy of a reaction, in which all the substances are at unit activity and at temperature  $T$ , is designated as  $\Delta F^\circ_T$ . The free energies of all elements and of  $\text{H}^+$  are taken as zero in their standard states.

(3) The relation between the free energy change for substances in their standard states and the equilibrium constant,  $K$ , is

$$-RT \ln_e K = \Delta F^\circ_T, \text{ or } -1364 \log_{10} K = \Delta F^\circ_{298^\circ\text{K}} \text{ (in cal.)}$$

where  $R$  is the gas constant and  $T$  the absolute temperature. The more general relation is:

$$-RT \ln K/Q = \Delta F_T$$

where  $Q$  has the same form as the equilibrium constant, but the concentrations refer to the values of the substances in their initial and final states. If these are unity, then  $Q$  is unity and the free energy is  $\Delta F^\circ$ .

*Example:* We may calculate the equilibrium constant for the reaction:  $\text{Cl}_{2(\text{aq.})} + \text{H}_2\text{O}_{(\text{liq.})} = \text{H}^+ + \text{Cl}^- + \text{HClO}_{(\text{sol.})}$ , from

the value  $\Delta F^\circ_{298} = 4600$ . Hence  $-\log_{10} K = 4600/1364$ ;  $K = (H^+)(Cl^-)(HClO)/(Cl_2) = 4.3 \times 10^{-4}$ .

(4) It follows from this relation that a large negative value for  $\Delta F$  means a large value for  $K$  or that the reaction as written is capable of proceeding to practical completion. It must be emphasized again, however, that free energies give no information as to the speed of the reaction.

(5) The reversible electromotive force,  $E$ , is a direct measure of the maximum available work or free energy of a chemical reaction:  $n \cdot 23066$ .  $E = -\Delta F$  where  $n$  is the number of Faradays of electricity which flow through the circuit, and  $\Delta F$  is given in calories.

*Example:*  $Ag^+ + \frac{1}{2}H_2 = H^+ + Ag$ ;  $E^\circ = 0.7995$ .

$$\Delta F^\circ = -0.7995 \times 23066 = -18440 \text{ cal.}$$

Since the free energies of  $H_2$ ,  $H^+$ , and  $Ag$  are zero by definition,  $F^\circ_{298}$  of  $Ag^+$  is 18440.

*Example:* To calculate the solubility product of  $AgCl$  at  $25^\circ C$ .

$$\begin{array}{rcl} Ag + Cl^- = AgCl + e^- & - & 0.2222 \text{ volt} \\ Ag = Ag^+ + e^- & - & 0.7995 \text{ " } \\ \hline Ag^+ + Cl^- = AgCl & & 0.5773 \text{ volt} \end{array}$$

Hence  $\Delta F^\circ = -0.5773 \times 23066 = -1365 \log 1/K$ , and  $K = 1.8 \times 10^{-10}$ .

TABLE OF STANDARD FREE ENERGIES OF FORMATION AT  $25^\circ C$ .

Values for many positive ions which may be calculated directly from the oxidation-reduction potentials have not been included, cf.  $Ag^+$ , P.(5) above.

SUBSTANCE	$\Delta F^\circ$	SUBSTANCE	$\Delta F^\circ$
$Al(OH)_3$	- 272,900	$BiO^+$	- 34,550
$H_2AlO_3^-$	- 256,000	$Be_2O_3(s)$	- 116,600
$Sb_2O_3(s)$	- 149,030	$BeOOH(s)$	- 87,800
$SbO^+$	- 42,000	$BrCl_4^-$	- 114,200
$SbO_2^-$	- 82,500	$H_3BO_3(s)$	- 220,600
$Sb_2O_5$	- 195,500	$H_2BO_3^-$	- 208,000
$As_2O_3(s)$	- 137,670	$BF_4^-$	- 335,900
$HAsO_2(aq)$	- 96,350	$Br_2(aq)$	977
$AsO_2^-$	- 83,770	$Br_2(g)$	755
$AsO^+$	- 39,260	$Br^-$	- 24,578
$H_3AsO_4(aq)$	- 183,930	$HBrO$	- 19,900
$BaCO_3(s)$	- 271,570	$BrO_3^-$	5,000
$BrO_2(s)$	- 138,000	$Cd(OH)_2(s)$	- 112,730
$Be_2O(OH)_2(s)$	- 305,610	$CdS(s)$	- 33,100
$Be_2O_3^{--}$	- 265,810	$CdCO_3(s)$	- 163,410

TABLE OF STANDARD FREE ENERGIES (*Cont'd*)

SUBSTANCE	$\Delta F^\circ$	SUBSTANCE	$\Delta F^\circ$
Ca(OH) <sub>2</sub> (s)	- 214,830	ICl <sub>2</sub> <sup>-</sup>	- 38,350
CaCO <sub>3</sub> (s)	- 207,430	IO <sub>3</sub> <sup>-</sup>	- 32,251
CO(g)	- 33,010	H <sub>5</sub> IO <sub>6</sub>	ca - 123,900
CO <sub>2</sub> (g)	- 94,450	IrCl <sub>6</sub> <sup>---</sup>	- 137,800
H <sub>2</sub> CO <sub>3</sub> (aq)	- 149,170	IrO <sub>2</sub>	- 28,000
HCO <sub>3</sub> <sup>-</sup>	- 140,490	Fe(OH) <sub>2</sub>	- 115,660
CO <sub>3</sub> <sup>---</sup>	- 126,390	FeCO <sub>3</sub>	- 161,260
HCN	26,340	Fe(OH) <sub>3</sub>	- 166,300
CN <sup>-</sup>	39,140	Fe <sub>2</sub> S <sub>3</sub>	- 55,000
Cl <sub>2</sub> (aq)	1,630	La(OH) <sub>3</sub>	ca - 303,800
Cl <sup>-</sup>	- 31,330	PbO(red)	- 45,100
ClO <sup>-</sup>	- 9,200	PbO(yellow)	- 44,956
HClO	- 19,110	PbO· $\frac{1}{2}$ H <sub>2</sub> O	- 63,721
HClO <sub>2</sub>	- 600	HPbO <sub>2</sub> <sup>-</sup>	- 80,800
ClO <sub>2</sub> <sup>-</sup>	2,100	Pb(OH) <sub>2</sub>	- 102,200
ClO <sub>3</sub> <sup>-</sup>	- 250	PbCl <sub>2</sub>	- 75,040
ClO <sub>4</sub> <sup>-</sup>	- 10,700	PbS	- 21,910
CrCl <sub>2</sub> <sup>+</sup>	- 114,100	PbSO <sub>4</sub>	- 159,500
Cr(OH) <sub>3</sub>	ca - 202,750	PbCO <sub>2</sub>	- 149,710
CrO <sub>2</sub> <sup>-</sup>	- 123,000	PbO <sub>2</sub>	- 52,020
Cr <sup>++</sup>	- 39,400	Mg(OH) <sub>2</sub>	- 193,300
CrO <sub>4</sub> <sup>---</sup>	- 171,400	MgO	- 136,370
HCrO <sub>4</sub> <sup>-</sup>	- 180,250	MgCO <sub>3</sub>	- 246,630
Cr <sub>2</sub> O <sub>7</sub> <sup>---</sup>	- 306,000	Mn(OH) <sub>2</sub>	- 143,100
CrO <sub>2</sub> Cl <sub>2</sub>	- 117,000	MnS	- 46,000
Co(OH) <sub>2</sub>	- 108,900	Mn(OH) <sub>3</sub>	ca - 190,000
CoS( $\alpha$ )	- 19,800	MnO <sub>4</sub> <sup>-</sup>	- 100,600
CoCO <sub>3</sub>	- 155,570	MnO <sub>2</sub>	- 102,900
Co(OH) <sub>3</sub>	- 142,000	MnO <sub>4</sub> <sup>---</sup>	- 113,100
Cu(OH) <sub>2</sub>	- 85,500	Hg <sub>2</sub> O	- 12,800
CuS	- 11,755	HgO(red)	- 13,940
CuCO <sub>3</sub>	- 123,930	Hg <sub>2</sub> Cl <sub>2</sub>	- 50,310
F <sup>-</sup>	- 65,700	HgO	- 13,940
HF(aq)	- 70,000	HgS	- 8,800
F <sub>2</sub> O(g)	9,500	MoO <sub>4</sub> <sup>---</sup>	- 208,000
Ga(OH) <sub>3</sub>	ca - 198,300	MoO <sub>3</sub>	- 157,600
H <sub>2</sub> GaO <sub>3</sub> <sup>-</sup>	ca - 178,000	Ni(OH) <sub>2</sub>	- 105,600
Au(g)	82,500	No(g)	20,660
AuI	- 760	N <sub>2</sub> O(g)	24,930
AuCl <sub>4</sub> <sup>-</sup>	- 56,200	No <sub>2</sub> (g)	12,274
HfO <sub>2</sub>	- 258,200	N <sub>2</sub> O <sub>4</sub> (g)	23,440
HfO <sup>++</sup>	- 212,100	NO <sub>3</sub> <sup>-</sup>	- 26,250
In <sub>2</sub> O <sub>3</sub>	- 21,800	HNO <sub>2</sub>	- 13,020
I <sub>2</sub> (g)	4,630	NO <sub>2</sub> <sup>-</sup>	- 8,450
I <sub>2</sub> (aq)	3,926	NH <sub>3</sub> (g)	- 3,940
I <sup>-</sup>	- 12,333	NH <sub>4</sub> OH(aq)	- 62,990
I <sub>3</sub> <sup>-</sup>	- 12,290	NH <sub>4</sub> <sup>+</sup>	- 18,960
HIO	- 23,330	OsO <sub>4</sub> (s)	- 69,400

TABLE OF STANDARD FREE ENERGIES (*Cont'd*)

SUBSTANCE	$\Delta F^\circ$	SUBSTANCE	$\Delta F^\circ$
O <sub>3</sub> (g)	39,400	H <sub>2</sub> S(g)	— 7,870
H <sub>2</sub> O(g)	— 54,636	H <sub>2</sub> S(aq)	— 6,520
OH <sup>-</sup>	— 37,585	HS <sup>-</sup>	2,950
H <sub>2</sub> O <sub>2</sub> (aq)	— 31,470	S <sup>--</sup>	23,420
HO <sub>2</sub> <sup>-</sup>	— 15,610	H <sub>2</sub> SO <sub>3</sub> (aq)	— 128,535
Pd(OH) <sub>2</sub>	ca — 70,500	SO <sub>4</sub> <sup>--</sup>	— 176,100
PdCl <sub>4</sub> <sup>--</sup>	ca — 96,000	HeTeO <sub>3</sub> (aq)	32,000
H <sub>3</sub> PO <sub>4</sub>	— 270,000	H <sub>2</sub> TeO <sub>3</sub> (aq)	— 115,700
H <sub>3</sub> PO <sub>3</sub> (aq)	— 204,000	TeO <sub>3</sub> <sup>--</sup>	— 110,100
PH <sub>3</sub> (g)	2,880	H <sub>6</sub> TeO <sub>6</sub>	— 241,100
Pt(OH) <sub>2</sub>	ca — 67,900	Tl(OH)	— 45,535
PtCl <sub>4</sub> <sup>--</sup>	— 91,600	TlCl	— 44,190
PtS	— 17,250	Tl(OH) <sub>3</sub>	— 123,000
KCl	— 97,555	ThO <sub>2</sub>	— 280,100
KBr	— 90,450	Sn(OH) <sub>2</sub>	— 115,950
ReO <sub>4</sub> <sup>-</sup>	— 202,800	HSnO <sub>2</sub> <sup>-</sup>	— 92,450
H <sub>2</sub> Se(aq)	16,720	SnS	— 21,250
H <sub>2</sub> SeO <sub>3</sub> (aq)	— 101,361	Sn(OH) <sub>6</sub> <sup>--</sup>	ca — 306,000
SeO <sub>3</sub> <sup>--</sup>	— 87,890	TiO <sub>2</sub> (rutile)	— 205,300
HSeO <sub>4</sub> <sup>-</sup>	— 107,840	WO <sub>3</sub>	— 171,400
SeO <sub>4</sub> <sup>--</sup>	— 105,120	WO <sub>4</sub> <sup>--</sup>	— 220,000
SiO <sub>2</sub> ( $\alpha$ quartz)	— 190,400	UO <sub>2</sub> <sup>++</sup>	— 226,800
SiO <sub>3</sub> <sup>--</sup>	ca — 215,000	UO <sub>2</sub>	— 242,200
Ag <sub>2</sub> O	— 2,590	V <sub>2</sub> O <sub>5</sub>	— 406,000
AgBr	— 22,900	Zn(OH) <sub>2</sub>	— 132,640
AgI(ppt)	— 15,810	ZnO <sub>2</sub> <sup>--</sup>	— 93,030
Ag <sub>2</sub> S	— 9,500	Zn(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup>	— 72,740
Ag <sub>2</sub> CO <sub>3</sub>	— 104,600	ZnS	— 43,200
NaOH(s)	— 90,475	ZnCO <sub>3</sub>	— 174,780
Na <sub>2</sub> CO <sub>3</sub>	— 250,800	ZrO <sub>2</sub>	— 245,400
SrCO <sub>3</sub>	— 271,900	ZrO <sup>++</sup>	— 198,100

## Appendix IV

### IONIZATION OF STRONG ELECTROLYTES

The freezing point lowering of a molal solution of a strong electrolyte such as sodium chloride is somewhat less than twice the molal freezing point lowering (cf. Hildebrand, *Prin. of Chem.*, p. 59) and the assumption was formerly made that the sodium chloride was only partially ionized. It is now believed that the sodium chloride is completely ionized in the sense that

TABLE I  
ACTIVITY COEFFICIENT OF TYPICAL ELECTROLYTES AT 25° C.

MOLALITY	0.01	0.05	0.10	1.0
KOH	0.90	0.82	0.80	0.76
AgNO <sub>3</sub>	0.90	0.77	0.72	0.40
KIO <sub>3</sub>	0.88	0.76	0.69	
BaCl <sub>2</sub>	0.72	0.56	0.49	0.39
CdCl <sub>2</sub>	0.47	0.28	0.21	0.06
K <sub>2</sub> SO <sub>4</sub>	0.71	0.52	0.43	
H <sub>2</sub> SO <sub>4</sub>	0.54	0.34	0.26	0.13
MgSO <sub>4</sub>	0.40	0.22	0.18	0.06
CuSO <sub>4</sub>	0.41	0.21	0.16	0.05
La(NO <sub>3</sub> ) <sub>3</sub>	0.57	0.39	0.33	
NaCl	0.90	0.82	0.78	0.66
NaNO <sub>3</sub>	0.90	0.82	0.77	0.55
ZnCl <sub>2</sub>	0.71	0.56	0.50	0.33
NH <sub>4</sub> Cl	0.88	0.79	0.74	0.57
CdSO <sub>4</sub>	0.40	0.21	0.17	0.04
NaI	0.91	0.86	0.83	0.80

the ions are capable of independent motion, and that the apparent non-ionization is due to the forces acting between an ion and its neighbors in general rather than its attachment to any particular ion. Since this force causes a departure of the ions from the behavior of perfect solutions, it is necessary to use a corrected con-



centration, called **activity**,  $a$ , in all thermodynamic relations, and the ratio of the activity to the concentration (molality) is defined as the **activity coefficient**,  $\gamma = a/c$ . At infinite dilution the force between the ions is zero, and the activity equals the concentration, i.e.,  $\gamma = 1$  (Fig. 1). As the concentration increases, the activity

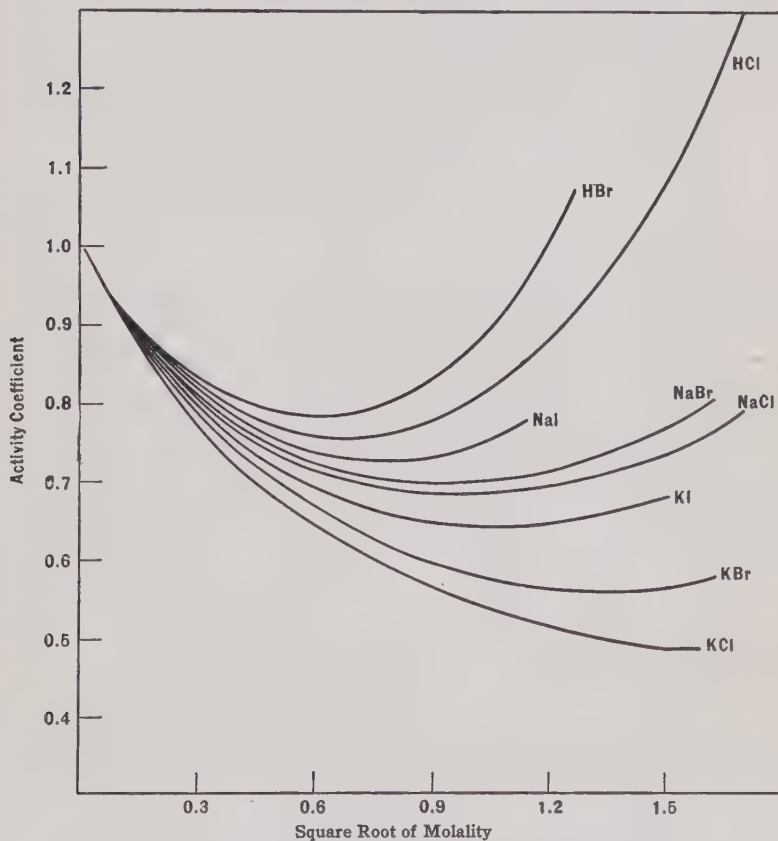


FIG. 1. Activity coefficient of hydrogen and alkali halides.

coefficient becomes less than unity, due to the attraction of the oppositely charged ions (Debye and Hückel theory), but at high concentrations other factors enter such as the force of repulsion between the large hydrated ions, or the change in hydration of the ions, and the coefficient may become greater than unity.

It is not possible to measure the activity of an ion of one sign

independent of the ion of opposite sign, i.e.,  $\text{Na}^+$  is not independent of  $\text{Cl}^-$  in  $\text{NaCl}$ ; hence the activity is determined as the mean of both ions, and the activity coefficient expressed as the mean activity divided by the mean molality. The mean activity and molality are defined in such a manner (cf. Lewis and Randall, *Thermodynamics*, p. 328) that the ratio approaches unity at infinite dilution for all types of salts.

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# Appendix V

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## CRYSTAL FORMS AND TYPES OF CRYSTAL LATTICE

A crystal is classified according to the **elements of symmetry** which it possesses. Symmetry is determined by the following operations required to bring the crystal into coincidence with its original position.

(a) **Rotation about an Axis.**—If a crystal can be revolved about an axis through its center so that similar faces recur  $n$  times in one rotation, it is said to possess  $n$  fold symmetry about this axis. Only axes of two-, three-, four-, and six-fold symmetry are known or in fact are possible with a system of particles at finite distances apart.

(b) **Reflection in a Plane.**—A crystal which may be divided by a plane into two parts, mirror images of each other, is said to possess symmetry about this plane.

(c) **Inversion about the Center.**—If every line drawn through the center cuts similar parallel faces on opposite sides of the center, the crystal is said to possess a center of symmetry.

(d) **Simultaneous Rotation and Reflection.**—If a crystal can be revolved about an axis so that  $n$  times in one rotation faces recur which are alternate mirror images, the crystal is said to possess an axis of composite symmetry. Only four- and six-fold axes of composite symmetry can occur.

**Crystal Classes.**—There are 31 possible combinations of these four types of symmetry and these, together with the crystal without any symmetry, constitute the 32 crystal types.

The 32 types are grouped into six **crystal systems** with the following characteristics:

(1) **Isometric or Cubic.**—This system includes all crystals having three interchangeable axes at right angles. All crystals have 4 axes of three-fold symmetry. One of the most important

forms is the cube which has 3 axes of four-fold symmetry, 4 axes of three-fold symmetry which also have six-fold composite symmetry, 6 axes of two-fold symmetry, nine planes of symmetry and a center of symmetry. Other forms are the octahedron, dodecahedron, and tetrahedron.

(2) **Tetragonal.**—One four-fold axis (may be four-fold composite axis) and two interchangeable axes at right angles to the principal axis and to each other. The tetragonal prism is a common form.

(3) **Hexagonal.**—One three-fold or six-fold axis of symmetry. Three interchangeable lateral axes of reference are generally employed which are perpendicular to the axes of symmetry and intersect each other at  $120^\circ$ . Hexagonal prisms, hexagonal bipyramids, and rhombohedra are common forms.



FIG. 1. Body-centered cubic. Structure of Cr, Fe (alpha), Li, Na, K, Mo, Ta, V, W.



FIG. 2. Face-centered cubic. Structure of Ag, Al, Au, Ca, Ce, Co (cubic), Cu, Fe (gamma), Ir, Ni, Pb, Pt, Th, A.



FIG. 3. Hexagonal close-packed. Structure of Be, Cd, Ce, Co, Hf, Mg, Os, Ti, Tl, Zn, Zr.

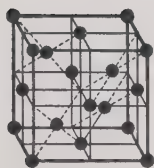


FIG. 4. Diamond type. Structure of C (diamond), Si, Sn (grey).

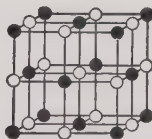


FIG. 5. Sodium chloride type. Structure of lithium, sodium and potassium halides: CaO, SiO, MgS, VN, NiO, CoO, FeO, AgCl, AgBr, PbS, MgO, CoF.



FIG. 6. Cesium chloride type. Structure of CsCl, CsBr, CsI, TlCl, TlBr, TlI.



FIG. 7. Zinc oxide type. Structure of  $\text{ZnO}$ ,  $\text{AgI}$ ,  $\text{TaN}$ ,  $\text{AlN}$ ,  $\text{BeO}$ .

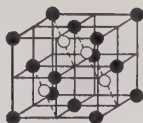


FIG. 8. Zinc sulfide (sphalerite) type. Structure of  $\text{ZnS}$ ,  $\text{HgS}$ ,  $\text{CuCl}$ ,  $\text{CuBr}$ ,  $\text{CuI}$ ,  $\text{AgI}$ .



FIG. 9. Cuprous oxide type. Structure of  $\text{Cu}_2\text{O}$ ,  $\text{Ag}_2\text{O}$ .

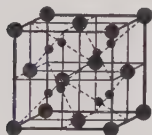


FIG. 10. Calcium fluoride type. Structure of  $\text{CaF}_2$ ,  $\text{Li}_2\text{S}$ ,  $\text{Li}_2\text{O}$ ,  $\text{Cu}_2\text{Se}$ ,  $\text{Na}_2\text{S}$ ,  $\text{BaF}_2$ ,  $\text{PbF}_2$ ,  $\text{SrF}_2$ ,  $\text{HgF}_2$ ,  $\text{ThO}_2$ ,  $\text{CdF}_2$ ,  $\text{CeO}_2$ ,  $\text{UO}_2$ ,  $\text{PrO}_2$ ,  $\text{SrCl}_2$ . Ratio of radius of  $M$  to radius of  $X > 0.6$ .



FIG. 11. Rutile type. Structure of  $\text{TiO}_2$ ,  $\text{PbO}_2$ ,  $\text{MnF}_2$ ,  $\text{TeO}_2$ ,  $\text{FeF}_2$ ,  $\text{ZnF}_2$ ,  $\text{CoF}_2$ ,  $\text{NiF}_2$ ,  $\text{SnO}_2$ ,  $\text{MgF}_2$ ,  $\text{NbO}_2$ ,  $\text{MoO}_2$ ,  $\text{WO}_2$ ,  $\text{IrO}_2$ ,  $\text{VO}_2$ ,  $\text{MnO}_2$ . Ratio of radius of  $M$  to radius of  $X < 0.6$ .

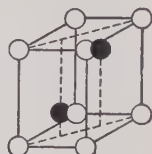


FIG. 12. Manganous hydroxide type. Structure of  $\text{Mn(OH)}_2$ ,  $\text{ZrS}_2$ ,  $\text{CdI}_2$ ,  $\text{Mg(OH)}_2$ ,  $\text{Ca(OH)}_2$ .

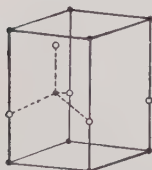


FIG. 13. Wurtzite,  $\text{ZnS}$ , type. Structure of  $\text{NH}_4\text{F}$ ,  $\text{BeO}$ ,  $\text{ZnO}$ ,  $\text{CdS}$ ,  $\text{MgTe}$ ,  $\text{CdSe}$ ,  $\text{AlN}$ .

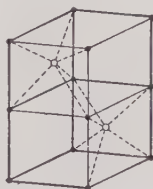


FIG. 14.  $\text{NiAs}$  type. Structure of  $\text{FeS}$ ,  $\text{CoS}$ ,  $\text{NiS}$ ,  $\text{FeSe}$ ,  $\text{CoSe}$ ,  $\text{CoTe}$ .

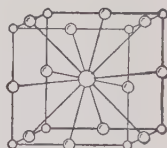


FIG. 15. Perowskit type. Structure of  $\text{CaTiO}_3$ ,  $\text{KIO}_3$ ,  $\text{CaZrO}_3$ ,  $\text{CaSnO}_3$ ,  $\text{LaAlO}_3$ ,  $\text{KMgF}_3$ .

This system is often divided so as to give a **Rhombohedral class**, crystals of which may be referred to 3 axes, all equal and all inclined unequally.

(4) **Orthorhombic**.—Crystals with three non-interchangeable axes of symmetry at right angles to each other. The rhombic prism and rhombic pyramid are common forms.

(5) **Monoclinic**.—Crystal with a single axis of symmetry but not three-, four-, or six-fold. Two additional axes of reference are chosen at right angles to the axis of symmetry and usually oblique to each other. A rhombic prism having a two-fold axis, a plane, and a center of symmetry is a common form.

(6) **Triclinic**.—Crystal possesses no direction of symmetry. Reference axes are non-interchangeable and in general at oblique angles. Two classes, with and without center of symmetry.



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## Appendix VI

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### QUALITATIVE ANALYSIS SCHEME

## BASIC CONSTITUENTS

### SEPARATION OF THE BASIC CONSTITUENTS INTO GROUPS

(From A. A. Noyes' *Qualitative Chemical Analysis*)

Solution in dilute nitric acid containing all the common basic constituents. Add $\text{NH}_4\text{Cl}$ .				
Precipitate: Silver-Group (Bi, Pb, Ag, Hg) as chlorides.	Filtrate: Saturate with $\text{H}_2\text{S}$ gas.			
	Precipitate: Copper-Group and Tin-Group as sulfides. Treat with $(\text{NH}_4)_2\text{S}_4$ .		Filtrate: Add $\text{NH}_4\text{OH}$ and $(\text{NH}_4)_2\text{S}$ .	
	Residue: Copper-Group (Hg, Pb, Bi, Cu, Cd), as sulfides.	Solution: Tin-Group (As, Sb, Sn), as ammonium sulfo-salts.	Precipitate: Aluminum-Group and Iron Group, as hydroxides and sulfides. Dissolve in acid, add $\text{NaOH}$ and $\text{Na}_2\text{O}_2$ .	
		Filtrate: Aluminum-Group (Al, Cr, Zn), as sodium salts.	Precipitate: Iron-Group (Mn, Fe, Co, Ni), as hydroxides.	Filtrate: Alkali-Group ( $\text{NH}_4$ , K, Na), as nitrates and chlorides.
ANALYSIS OF THE SILVER GROUP				
Precipitate: $\text{BiOCl}$ , $\text{PbCl}_2$ , $\text{AgCl}$ , $\text{Hg}_2\text{Cl}_2$ . Treat with $\text{HCl}$ .				
Solution $\text{BiCl}_3$ . Evaporate, pour into water.	Residue: $\text{PbCl}_2$ , $\text{AgCl}$ , $\text{Hg}_2\text{Cl}_2$ . Treat with hot water.			
	Solution: $\text{PbCl}_2$ . Add $\text{H}_2\text{SO}_4$ .		Residue: $\text{AgCl}$ , $\text{Hg}_2\text{Cl}_2$ . Pour $\text{NH}_4\text{OH}$ through the filter.	
	Precipitate: $\text{PbSO}_4$ .		Black residue: Hg and $\text{NH}_2\text{HgCl}$ .	Solution: $(\text{NH}_4)_2\text{AgCl}$ . Add $\text{HNO}_3$ .
Precipitate: $\text{BiOCl}$ .	White precipitate: $\text{AgCl}$ .			

# SEPARATION OF THE COPPER AND TIN GROUPS

Hydrogen sulfide precipitate: HgS, PbS, Bi <sub>2</sub> S <sub>3</sub> , CuS, CdS, As <sub>2</sub> S <sub>3</sub> , As <sub>2</sub> S <sub>6</sub> , Sb <sub>2</sub> S <sub>3</sub> , Sb <sub>2</sub> S <sub>6</sub> , SnS, SnS <sub>2</sub> . Treat with ammonium polysulfide.		
Residue: HgS, PbS, Bi <sub>2</sub> S <sub>3</sub> , CuS, CdS.	Solution: (NH <sub>4</sub> ) <sub>3</sub> AsS <sub>4</sub> , (NH <sub>4</sub> ) <sub>3</sub> SbS <sub>4</sub> , (NH <sub>4</sub> ) <sub>2</sub> SnS <sub>3</sub> . Add HCl.	
	Precipitate: As <sub>2</sub> S <sub>6</sub> , Sb <sub>2</sub> S <sub>6</sub> , SnS <sub>2</sub> .	Filtrate: NH <sub>4</sub> Cl. Reject.

## ANALYSIS OF THE COPPER GROUP

Residue from Ammonium Sulfide Treatment : HgS, PbS, Bi <sub>2</sub> S <sub>3</sub> , CuS, CdS. Boil with HNO <sub>3</sub> .				
Solution: Pb, Bi, Cu, Cd as nitrates. Add H <sub>2</sub> SO <sub>4</sub> , evaporate, add water.				
Residue: HgS. Add Br <sub>2</sub> solution.	Precipitate: PbSO <sub>4</sub> . Dissolve in NH <sub>4</sub> Ac. K <sub>2</sub> CrO <sub>4</sub> .	Filtrate: add NH <sub>4</sub> OH.		
		Precipitate: Bi(OH) <sub>3</sub> . Add Na <sub>2</sub> SnO <sub>2</sub> .		
		Black residue: Bi.		
		Yellow precipitate: PbCrO <sub>4</sub> .		
		Filtrate: Cu(NH <sub>3</sub> ) <sub>4</sub> SO <sub>4</sub> , Cd(NH <sub>3</sub> ) <sub>4</sub> SO <sub>4</sub> .		
Residue: Sulfur.	Solution: HgBr <sub>2</sub> . Add SnCl <sub>2</sub> .	To a small part add HAc and K <sub>4</sub> Fe(CN) <sub>6</sub> . To the remainder add KCN and H <sub>2</sub> S.		
	White or grey precipitate: Hg <sub>2</sub> Cl <sub>2</sub> or Hg.	Red precipitate: Cu <sub>2</sub> Fe-(CN) <sub>6</sub> . White precipitate: Cd <sub>2</sub> Fe(CN) <sub>6</sub> .		
		Yellow precipitate: CdS. Solution: K <sub>3</sub> Cu(CN) <sub>4</sub> .		

# ANALYSIS OF THE TIN GROUP

Precipitate from Ammonium Sulfide Solution: $As_2S_5$ , $Sb_2S_3$ , $SnS_2$ . Heat with 10 cc. 12 normal HCl.		
Solution: $SbCl_3$ , $SnCl_4$ . Dilute to 50 cc., heat, and pass in $H_2S$ .	Solution: $SnCl_4$ . Cool, dilute, pass in $H_2S$ .	Residue: $As_2S_5$ . Dissolve in HCl and $KClO_3$ .
Orange precipitate: $Sb_2S_3$ . Dissolve in HCl, add Sn and Pt.	Yellow precipitate: $SnS_2$ . Evaporate without filtering, add Pb, boil.	Solution: $H_3AsO_4$ . Add $NH_4OH$ , $NH_4Cl$ , and $MgCl_2$ .
Black deposit: Sb. Treat with $NaClO$ .	Solution: $SnCl_2$ . Add $HgCl_2$ .	White precipitate: $MgNH_4AsO_4$ . Dissolve in HCl and add $H_2S$ .
Black deposit: Sb.	White precipitate: $Hg_2Cl_2$ .	Yellow precipitate: $As_2S_6$ , $As_2S_3$ , and S.

## SEPARATION OF THE ALUMINUM AND IRON GROUPS

The Ammonium Hydroxide and Ammonium Sulfide Precipitate: $Al(OH)_3$ , $Cr(OH)_3$ , $FeS$ , $ZnS$ , $MnS$ , $CoS$ , $NiS$ . Dissolve in HCl and $HNO_3$ , add $NaOH$ .	
Precipitate: $Fe(OH)_3$ , $Mn(OH)_2$ , $Co(OH)_2$ , $Ni(OH)_2$ . Solution: $NaAlO_2$ , $NaCrO_2$ , $Na_2ZnO_2$ . Add $Na_2O_2$ and filter.	
Filtrate: $NaAlO_2$ , $Na_2CrO_4$ , $Na_2ZnO_2$ .	Precipitate: $Fe(OH)_3$ , $MnO(OH)_2$ , $Co(OH)_3$ , $Ni(OH)_2$ .

### ANALYSIS OF THE ALUMINUM GROUP

Filtrate from the Sodium Hydroxide and Peroxide Treatment: $\text{Na}_2\text{ZnO}_2$ , $\text{NaAlO}_2$ , $\text{Na}_2\text{CrO}_4$ . Acidify with $\text{HNO}_3$ and add $\text{NH}_4\text{OH}$ .		
Precipitate: $\text{Al}(\text{OH})_3$ . Dissolve in $\text{HNO}_3$ . Add $\text{Co}(\text{NO}_3)_2$ , evaporate, ignite.	Filtrate: add $\text{HAc}$ and $\text{BaCl}_2$ .	Filtrate: Zinc salt. Pass in $\text{H}_2\text{S}$ .  White precipitate: $\text{ZnS}$ . Dissolve in $\text{HNO}_3$ . Add $\text{Co}(\text{NO}_3)_2$ and $\text{Na}_2\text{CO}_3$ , ignite.  Green residue: $\text{CoZnO}_2$ .
Blue residue: $\text{Co}(\text{AlO}_2)_2$ .	Precipitate: $\text{BaCrO}_4$ . Dissolve in $\text{HCl}$ and $\text{H}_2\text{SO}_3$ , evaporate.	
	Green color: $\text{CrCl}_3$ .	

### ANALYSIS OF THE IRON GROUP

Precipitate produced by sodium hydroxide and peroxide: A. Phosphate absent: $\text{MnO}(\text{OH})_2$ , $\text{Fe}(\text{OH})_3$ , $\text{Co}(\text{OH})_3$ , $\text{Ni}(\text{OH})_2$ , $\text{Zn}(\text{OH})_2$ . B. Phosphate present: Also $\text{BaCO}_3$ , $\text{SrCO}_3$ , $\text{CaCO}_3$ , $\text{MgCO}_3$ , $\text{FePO}_4$ , $\text{Ca}_3(\text{PO}_4)_2$ , etc. Dissolve in $\text{HNO}_3$ and $\text{H}_2\text{O}_2$ , evaporate, heat with $\text{HNO}_3$ and $\text{KClO}_3$ .		
Precipitate: $\text{MnO}_2$ . Add $\text{HNO}_3$ and bismuth peroxide.	Solution: Test a portion for a phosphate with $(\text{NH}_4)_2\text{MoO}_4$ . A. Phosphate absent: add $\text{NH}_4\text{OH}$ . B. Phosphate present: add $\text{NH}_4\text{Ac}$ and $\text{FeCl}_3$ , dilute and boil.	
Violet color: $\text{HMnO}_4$ .	Precipitate: A. $\text{Fe}(\text{OH})_3$ . B. Basic ferric acetate and $\text{FePO}_4$ .	Filtrate: add $\text{NH}_4\text{OH}$ , pass in $\text{H}_2\text{S}$ .  Precipitate: $\text{ZnS}$ , $\text{CoS}$ , $\text{NiS}$ .  Filtrate: A. Ammonium salts. Reject. B. Ba, Ca, Sr, Mg. Treat with Alkali-Earth group.

# SEPARATION OF ZINC, NICKEL, AND COBALT

Hydrogen sulfide precipitate: ZnS, NiS, CoS. Treat with dil. HCl.				
Solution: ZnCl <sub>2</sub> , NiCl <sub>2</sub> , CoCl <sub>2</sub> , add NaOH and Na <sub>2</sub> O <sub>2</sub> .			Residue: NiS, CoS. Dissolve in HCl and HNO <sub>3</sub> .	
Filtrate: Na <sub>2</sub> ZnO <sub>2</sub> . Add HAc and H <sub>2</sub> S.				
White precipitate: ZnS.			Precipitate: Ni(OH) <sub>2</sub> , Co(OH) <sub>3</sub> , add HCl, evaporate.	
			Residue: NiCl <sub>2</sub> , CoCl <sub>2</sub> , add HCl and ether.	
			Yellow residue: NiCl <sub>2</sub> . Dissolve in water, add tartaric acid, NaOH and H <sub>2</sub> S.	
			Brown coloration: presence of nickel.	
ANALYSIS OF THE ALKALINE-EARTH GROUP				
Ammonium carbonate precipitate: BaCO <sub>3</sub> , SrCO <sub>3</sub> , CaCO <sub>3</sub> , MgCO <sub>3</sub> , (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> . Dissolve in HAc, add NH <sub>4</sub> Ac and K <sub>2</sub> CrO <sub>4</sub> .				
Precipitate: BaCrO <sub>4</sub> . Dissolve in HCl, evaporate			Filtrate: add NH <sub>4</sub> OH and alcohol.	
Test in flame.	Add HAc, NH <sub>4</sub> Ac, and K <sub>2</sub> CrO <sub>4</sub> .		Precipitate: SrCrO <sub>4</sub> . Treat with (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> .	
			Filtrate: Ca and Mg salts. Add (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .	
Green color: Ba.	Precipitate: BaCrO <sub>4</sub> .		Residue: SrCO <sub>3</sub> . Dissolve in HAc. Add CaSO <sub>4</sub> .	
Precipitate: add NH <sub>4</sub> OH and Na <sub>2</sub> HPO <sub>4</sub> . Precipitate: MgNH <sub>4</sub> PO <sub>4</sub> .				
			Precipitate: SrSO <sub>4</sub> . Precipitate: CaSO <sub>4</sub> .	



# ANALYSIS OF THE ALKALI GROUP

Filtrate from Ammonium Carbonate precipitate: $\text{NH}_4$ , Na, K salts. Evaporate and ignite the residue.			
Vapor: $\text{NH}_4$ salts.	Residue: KCl, NaCl. Add $\text{HClO}_4$ , evaporate, add alcohol.		
	Residue: $\text{KClO}_4$ . Dissolve in hot water, add $\text{Na}_2\text{Co}(\text{NO}_2)_6$ .	Solution: $\text{NaClO}_4$ . Saturate with HCl gas.	
	Yellow precipitate: $\text{K}_2\text{NaCo}(\text{NO}_2)_6$ .	Precipitate: NaCl. Dissolve in water, add $\text{KSb}(\text{OH})_6$ .	
	Crystalline precipitate: $\text{NaSb}(\text{OH})_6$ .		

## ACIDIC CONSTITUENTS

### DETECTION OF THE READILY VOLATILE ACIDIC CONSTITUENTS

Heat the substance with dilute  $\text{H}_2\text{SO}_4$ .

Vapors:  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{NO}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ,  $\text{HCN}$ . Expose to the vapors.

$\text{Ba}(\text{OH})_2$ solution.	PbAc paper.	Starch and KI paper.	$\text{Fe}(\text{OH})_2$ or $\text{Fe}(\text{OH})_3$ and NaOH on paper.
White turbidity: $\text{BaCO}_3$ or $\text{BaSO}_3$ . (Shows carbonate, sulfite, or thiosulfate.)	Black color: PbS. (Shows sulfide.)	Blue color: $\text{I}_2$ . (Shows nitrite, hypochlorite, chlorate, bromate, or iodide.)	Formation of $\text{Na}_4\text{Fe}(\text{CN})_6$ . Dip in HCl.
			Blue color: $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ . (Shows cyanide.)

# DETECTION OF THE ACIDIC CONSTITUENTS PRECIPITATED FROM ACID SOLUTIONS BY BARIUM AND SILVER SALTS

To a $\text{HNO}_3$ solution of the substance add $\text{BaCl}_2$ .			
Precipitate: $\text{BaSO}_4$ . (Shows sulfite.)	Filtrate: add $\text{Br}_2$ .		To a $\text{HNO}_3$ solution of the substance add $\text{Cd}(\text{NO}_3)_2$ .
	Precipitate: $\text{BaSO}_4$ . (Shows sulfite.)	Filtrate: add $\text{NH}_4\text{Ac}$ .	
	Yellow precipitate: $\text{BaCrO}_4$ . (Shows chromate.)	Filtrate: add $\text{CaCl}_2$ . Precipitate: $\text{CaF}_2$ . (Shows fluoride.)	
Yellow precipitate: $\text{CdS}$ . (Shows sulfide.)			Filtrate: Add $\text{AgNO}_3$ .
			Precipitate: $\text{AgCl}$ , $\text{AgBr}$ , $\text{AgI}$ , $(\text{AgCN})_2$ , $\text{AgSCN}$ . (Shows halides, cyanide or thiocyanates.)
			Filtrate: $\text{AgClO}_3$ , $\text{AgBrO}_3$ . Add $\text{H}_2\text{SO}_3$ .
			Precipitate: $\text{AgCl}$ , $\text{AgBr}$ . (Shows chlorate or bromate.)

## DETECTION OF PHOSPHATE AND THE SEPARATE HALIDES

To portions of the $\text{HNO}_3$ solution of the substance.			
Add $(\text{NH}_4)_2\text{MoO}_4$ .	Add $\text{FeCl}_3$ .	Add NaAc, HAc, $\text{KMnO}_4$ , and $\text{CHCl}_3$ .	
Yellow precipitate: $(\text{NH}_4)_3\text{PO}_4$ , $12\text{MoO}_3$ . (Shows phosphate.)	Red color: $\text{Fe}(\text{SCN})_3$ . (Shows thiocyanate.)	Chloroform layer, purple: $\text{I}_2$ . (Shows iodide.)	Water layer: add $\text{H}_2\text{SO}_4$ , more $\text{KMnO}_4$ and $\text{CHCl}_3$ .
			Chloroform layer, orange: $\text{Br}_2$ . (Shows bromide.)
			Water layer: Boil out the $\text{Br}_2$ , add $\text{HNO}_3$ and $\text{AgNO}_3$ .
		Precipitate: $\text{AgCl}$ . (Shows chloride.)	

# Appendix VII

## STRUCTURE OF MOLECULES AND IONS

LINEAR	$\text{HgCl}_2(\text{g})$ , $\text{HgBr}_2(\text{g})$ , $\text{HgI}_2(\text{g})$ , $\text{CO}_2$ , $\text{C}_3\text{O}_2$ , $\text{SCO}$ , $\text{C}_4\text{H}_2$ , $\text{CH}_3\text{CN}$ , $\text{CH}_3\text{NC}$ , $\text{CS}_2$ , $\text{C}_2\text{N}_2$ , $\text{H}_2\text{CN}_2$ , $\text{N}_3^-$ , $\text{NNO}$ , $\text{CH}_3\text{MgI}$ , $\text{FHF}^-$ , $\text{BrIBr}^-$ , $\text{ClIBr}^-$ , $\text{AuCl}_2^-$ , $\text{Ag}(\text{CN})_2^-$ , $\text{BO}_2^-$ , $\text{BeO}_2^{--}$ , $\text{I}_3^-$ (with 3 electron pairs about center I?).
PLANE TRIANGULAR	$\text{BCl}_3$ , $\text{B}(\text{CH}_3)_3$ , $\text{NO}_3^-$ , $\text{CO}_3^{--}$ , $\text{C}(\text{NH}_2)_3^+$ , $\text{SO}_3$ , $\text{CuCl}_3^-$ , $\text{Ni}(\text{CN})_3^-$ , $\text{H}_2\text{CO}$ , $\text{OCCl}_2$ ( $\text{Cl}-\text{C}-\text{Cl}$ , $117^\circ$ ), $\text{SCCl}_2$ ( $\text{Cl}-\text{C}-\text{Cl}$ , $116^\circ$ ), $\text{CH}_3\text{NO}_2$ ( $\text{O}-\text{N}-\text{O}$ , $127^\circ$ ).
PLANAR	$\text{C}_6\text{H}_6$ , $(\text{HCOOH})_2(\text{g})$ , $\text{CH}_3\text{NNCH}_3(\text{g})$ .
BENT OR V-SHAPED	$\text{FOF}$ ( $100^\circ$ ), $\text{ClOCl}$ ( $115^\circ$ ), $\text{OCIO}$ ( $125^\circ$ ), $\text{ClO}_2^-$ ( $114^\circ$ ), $\text{ONCl}$ ( $125^\circ$ ), $\text{ONBr}$ , $\text{ClSCl}$ ( $103^\circ$ ), $(\text{CH}_3)_2\text{O}$ ( $111^\circ$ ), $\text{O}_3$ , $(\text{CH}_3)_2\text{S}$ , $\text{ONO}$ ( $110-120^\circ$ ), $\text{NO}_2^-$ ( $132^\circ$ ), $\text{OSO}$ ( $122^\circ$ ), $\text{H}_2\text{S}$ ( $92^\circ$ ), $\text{H}_2\text{O}$ ( $105^\circ$ ).
PYRAMIDAL	$\text{PF}_3$ ( $\text{F}-\text{P}-\text{F}$ , $104^\circ$ ), $\text{PCl}_3$ ( $\text{Cl}-\text{P}-\text{Cl}$ , $101^\circ$ ), $\text{PBr}_3$ ( $\text{Br}-\text{P}-\text{Br}$ , $100^\circ$ ), $\text{PI}_3$ ( $\text{I}-\text{P}-\text{I}$ , $98^\circ$ ), $\text{AsF}_3$ , $\text{AsCl}_3$ ( $\text{Cl}-\text{As}-\text{Cl}$ , $103^\circ$ ), $\text{AsBr}_3$ ( $\text{Br}-\text{As}-\text{Br}$ , $100^\circ$ ), $\text{AsI}_3$ ( $\text{I}-\text{As}-\text{I}$ , $100^\circ$ ), $\text{SbCl}_3$ ( $\text{Cl}-\text{Sb}-\text{Cl}$ , $104^\circ$ ), $\text{SbBr}_3$ ( $\text{Br}-\text{Sb}-\text{Br}$ , $96^\circ$ ), $\text{SbI}_3$ ( $\text{I}-\text{Sb}-\text{I}$ , $98^\circ$ ), $\text{P}(\text{CH}_3)_3$ ( $\text{C}-\text{P}-\text{C}$ , $100^\circ$ ), $\text{PFCl}_2$ ( $\text{Cl}-\text{P}-\text{Cl}$ , $102^\circ$ ), $\text{N}(\text{CH}_3)_3$ ( $\text{C}-\text{N}-\text{C}$ , $108^\circ$ ), $\text{NH}_3$ ( $\text{H}-\text{N}-\text{H}$ , $108^\circ$ ), $\text{SO}_3^{--}$ ( $\text{O}-\text{S}-\text{O}$ , $111^\circ$ ), $\text{ClO}_3^-$ ( $\text{O}-\text{Cl}-\text{O}$ , $107^\circ$ ).
SQUARE PLANAR	$\text{XY}_4$ ions and molecules of $\text{Pd}^{++}$ , $\text{Pt}^{++}$ , $\text{Cu}^{++}$ , $\text{Ag}^{++}$ , $\text{Au}^{+++}$ , $\text{Ni}^{++}$ (if diamagnetic), $\text{ICl}_4^-$ .
TETRA- HEDRAL	$\text{P}_4$ , $\text{As}_4$ , $\text{Ni}(\text{CO})_4$ , $\text{NH}_4^+$ , $\text{BF}_4^-$ , $\text{BeF}_4^{-2}$ , $\text{Li}(\text{NH}_3)_4$ , $\text{SiO}_4^{-4}$ , $\text{AlO}_4^{-5}$ , $\text{SO}_4^{-2}$ , $\text{PO}_4^{-3}$ , $\text{H}_2\text{PO}_2^-$ , $\text{ClO}_4^-$ ,

$\text{CrO}_4^{--}$ ,  $\text{MnO}_4^-$ ,  $\text{MnO}_4^{--}$ ,  $\text{SnBr}_4$ ,  $\text{Pb}(\text{C}_2\text{H}_5)_4$ ,  $\text{TiCl}_4$ ,  $\text{GeCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{Cu}(\text{CN})_4^{---}$ , and other  $\text{Cu}^+$  complex ions,  $\text{Ni}(\text{H}_2\text{O})_4^{++}$ ,  $\text{Ni}(\text{N}_2\text{H}_4)_2^{++}$  and other paramagnetic complex ions of  $\text{Ni}^{++}$ ,  $(\text{CH}_3)_3\text{PtCl}$ , and  $\text{Pt}^{+4}$  complex ions,  $\text{M}(\text{CM})_4^{--}$  when M is Zn, Cd, or Hg,  $\text{SnS}_4^{-4}$ ,  $\text{AsS}_4^{-3}$ ,  $\text{CCl}_4$  and all carbon compounds with four single bonds,  $\text{H}_2\text{Fe}(\text{CO})_4$ .

TRIGONAL  
BIPYRAMID

$\text{PCl}_5$ ,  $\text{PF}_5$ ,  $\text{PF}_3\text{Cl}_2$ ,  $\text{MoCl}_5$ ,  $(\text{CH}_3)_3\text{SbX}_2$ .

SQUARE  
PYRAMID

$\text{IF}_5$  (?).

OCTA-  
HEDRAL

In general, all  $\text{XY}_6$  compounds and complex ions. In  $\text{UF}_6$ ,  $\text{WF}_6$ ,  $\text{MoF}_6$  (as gases) the M-F distances of the three axes are different. In  $\text{MoS}_2$  (crystal) six sulfur atoms form a triangular prism about a molybdenum atom.

SEVEN-  
CORNERED  
POLYHEDRON

$\text{ZrF}_6^{---}$ ,  $\text{IF}_7$  (?).

HEXADRAL  
(CUBE) OR  
SQUARE AR-  
CHIMEDEAN  
ANTIPRISM

$\text{W}(\text{CN})_8^{-4}$ ,  $\text{Mo}(\text{CN})_8^{-4}$ , and  $\text{Ca}(\text{C}_2\text{H}_5\text{OH})_8^{++}$  probably the former.  $(\text{ZrF}_8)^{-4}$  (?),  $(\text{TaF}_8)^{-3}$  (?).

# Appendix VIII

## DENSITY OF WATER

### DENSITY OF WATER IN GRAMS PER CUBIC CENTIMETER

t° C.	DENSITY	t° C.	DENSITY	t° C.	DENSITY
0	0.999867	16	0.998969	32	0.995052
1	0026	17	8801	33	0.994728
2	9968	18	8621	34	4397
3	9992	19	8430	35	4058
4	1.000000	20	8229	36	0.993711
5	0.999992	21	8017	37	3356
6	9968	22	0.997795	38	0.992993
7	9929	23	7563	39	2622
8	9876	24	7321	40	0.992244
9	9808	25	7069	50	0.98804
10	9727	26	0.996808	60	0.98321
11	9632	27	6538	70	0.97778
12	9524	28	0.996258	80	0.97180
13	9404	29	0.995969	90	0.96531
14	0.999271	30	5672	100	0.95835
15	9126	31	5366	150	0.9173
				200	0.8628

### APPARENT DENSITY OF WATER, WHEN WEIGHED IN AIR WITH BRASS WEIGHTS, IN GRAMS PER CUBIC CENTIMETER

t° C.	DENSITY	t° C.	DENSITY	t° C.	DENSITY
15	0.99805	20	0.99718	25	0.99604
16	.99790	21	.99697	26	.99579
17	.99774	22	.99676	27	.99552
18	.99756	23	.99653	28	.99524
19	.99738	24	.99629	29	.99496
				30	.99466

# Appendix IX

## DENSITY OF MERCURY

DENSITY OF MERCURY IN GRAMS PER CUBIC CENTIMETER

t° C.	DENSITY	t° C.	DENSITY	t° C.	DENSITY
— 20	13.6450	15	13.5584	45	13.4849
— 10	6202	16	5560	50	4727
— 5	6078	17	5535	55	4605
0	5955	18	5511	60	4484
1	5930	19	5486	65	4362
2	5905	20	5461	70	4241
3	5880	21	5437	75	4120
4	5856	22	5412	80	3999
5	5831	23	5388	85	3878
6	5806	24	5363	90	3757
7	5782	25	5339	95	3637
8	5757	26	5314	100	3516
9	5732	27	5290	110	328
10	5708	28	5265	150	232
11	5683	29	5241	200	113
12	5658	30	5216	300	12.8760
13	5634	35	5094	400	6380
14	5609	40	4971	500	3950



# Appendix X

## EQUILIBRIUM PRESSURE OF WATER — WATER VAPOR

PRESSURE IN MM. OF MERCURY

(Cf. also Fig. 2, Chap. III)

t° C.	mm.	t° C.	mm.	t° C.	mm.
0	4.5687	39	51.997	78	327.05
1	4.9091	40	54.865	79	340.73
2	5.2719	41	57.870	80	354.87
3	5.6582	42	61.017	81	369.51
4	6.0693	43	64.310	82	384.64
5	6.5067	44	67.757	83	400.29
6	6.9718	45	71.362	84	416.47
7	6.4660	46	75.131	85	433.19
8	7.9909	47	79.071	86	450.47
9	8.5484	48	83.188	87	468.32
10	9.1398	49	87.488	88	486.76
11	9.7671	50	91.978	89	505.81
12	10.432	51	96.664	90	525.47
13	11.137	52	101.55	91	545.77
14	11.884	53	106.65	92	566.71
15	12.674	54	111.97	93	588.33
16	13.510	55	117.52	94	610.64
17	14.395	56	123.29	95	633.66
18	15.330	57	129.31	96	657.40
19	16.319	58	135.58	97	681.88
20	17.363	59	142.10	98	707.13
21	18.466	60	148.88	99	733.16
22	19.630	61	155.95	100	760.00
23	20.858	62	163.29	101	787.59
24	22.152	63	170.92	102	816.01
25	23.517	64	178.86	103	845.28
26	24.956	65	187.10	104	875.41
27	26.471	66	195.67	110	1075.37
28	28.065	67	204.56	120	1491.28
29	29.744	68	213.79	130	2030.28
30	31.510	69	223.37	140	2717.63
31	33.366	70	233.31	150	3581.2
32	35.318	71	243.62	160	4651.6
33	37.369	72	254.30	170	5961.7
34	39.523	73	265.38	180	7546.4
35	41.784	74	276.87	190	9442.7
36	44.158	75	288.76	200	11689.0
37	46.648	76	301.09	209	14042.5
38	49.259	77	313.85		

# Appendix XI

## SOLUBILITY PRODUCTS AND ACID IONIZATION CONSTANTS

### Bromides

CuBr  
PbBr<sub>2</sub>  
Hg<sub>2</sub>Br<sub>2</sub>  
AgBr  
TlBr

### K

$5.3 \times 10^{-9}$  *Fluorides*  
 $6.3 \times 10^{-6}$  BaF<sub>2</sub>  
 $5.2 \times 10^{-23}$  CaF<sub>2</sub>  
 $3.3 \times 10^{-13}$  MgF<sub>2</sub>  
 $3.6 \times 10^{-6}$  PbF<sub>2</sub>  
SrF<sub>2</sub>

$1.7 \times 10^{-6}$   
 $3.4 \times 10^{-11}$   
 $6.4 \times 10^{-9}$   
 $3.7 \times 10^{-8}$   
 $3 \times 10^{-9}$

### Carbonates

BaCO<sub>3</sub>  
CdCO<sub>3</sub>  
CaCO<sub>3</sub>  
CoCO<sub>3</sub>  
CuCO<sub>3</sub>  
FeCO<sub>3</sub>  
PbCO<sub>3</sub>  
MgCO<sub>3</sub>·3H<sub>2</sub>O  
MnCO<sub>3</sub>  
Hg<sub>2</sub>CO<sub>3</sub>  
NiCO<sub>3</sub>  
Ag<sub>2</sub>CO<sub>3</sub>  
SrCO<sub>3</sub>  
ZnCO<sub>3</sub>

$4.9 \times 10^{-9}$  *Hydroxides*

$2.5 \times 10^{-14}$  Al(OH)<sub>3</sub>  
 $4.8 \times 10^{-9}$  Sb<sub>2</sub>O<sub>3</sub>(SbO<sup>+</sup>, OH<sup>-</sup>)  
 $1.0 \times 10^{-12}$  AsOOH(AsO<sup>+</sup>, OH<sup>-</sup>)  
 $1.4 \times 10^{-10}$  Ba(OH)<sub>2</sub>·8H<sub>2</sub>O  
 $2.1 \times 10^{-11}$  Be<sub>2</sub>O(OH)<sub>2</sub>(2Be<sup>++</sup>, 4OH<sup>-</sup>)  
 $1.5 \times 10^{-13}$  BiOOH(BiO<sup>+</sup>, OH<sup>-</sup>)  
 $1 \times 10^{-5}$  Cd(OH)<sub>2</sub>  
 $8.8 \times 10^{-11}$  Ca(OH)<sub>2</sub>  
 $9 \times 10^{-17}$  Cr(OH)<sub>3</sub>  
 $1.4 \times 10^{-7}$  Co(OH)<sub>2</sub>  
 $8.2 \times 10^{-12}$  Cu<sub>2</sub>O(Cu<sup>+</sup>, OH<sup>-</sup>)  
 $9.4 \times 10^{-10}$  Cu(OH)<sub>2</sub>  
 $6 \times 10^{-11}$  Ga(OH)<sub>3</sub>  
Au<sub>2</sub>O<sub>3</sub>(Au<sup>+++</sup>, 3OH<sup>-</sup>)  
HfO(OH)<sub>2</sub>(HfO<sup>++</sup>, 2OH<sup>-</sup>)

$1.9 \times 10^{-33}$   
 $10^{-17}$   
 $5 \times 10^{-15}$   
 $5 \times 10^{-3}$   
 $1 \times 10^{-40}$   
 $1 \times 10^{-12}$   
 $1.2 \times 10^{-14}$   
 $7.9 \times 10^{-6}$   
 $6.7 \times 10^{-31}$   
 $2 \times 10^{-16}$   
 $1.2 \times 10^{-15}$   
 $5.6 \times 10^{-20}$   
 $5 \times 10^{-37}$   
 $8.5 \times 10^{-46}$   
 $10^{-25}$

### Chlorides

CuCl  
PbCl<sub>2</sub>  
Hg<sub>2</sub>Cl<sub>2</sub>  
AgCl  
TlCl  
BiOCl(BiO<sup>+</sup>, Cl<sup>-</sup>)

$1.8 \times 10^{-7}$  Fe(OH)<sub>2</sub>  
 $1.7 \times 10^{-5}$  Fe(OH)<sub>3</sub>  
 $1.1 \times 10^{-18}$  La(OH)<sub>3</sub>  
 $1.7 \times 10^{-10}$  Pb(OH)<sub>2</sub>  
 $1.9 \times 10^{-4}$  Mg(OH)<sub>2</sub>  
 $7 \times 10^{-11}$  Mn(OH)<sub>2</sub>  
Hg<sub>2</sub>O(Hg<sub>2</sub><sup>++</sup>, 2OH<sup>-</sup>)  
HgO(Hg<sup>++</sup>, 2OH<sup>-</sup>)

$1.6 \times 10^{-15}$   
 $4 \times 10^{-38}$   
 $10^{-20}$   
 $2.8 \times 10^{-16}$   
 $5.5 \times 10^{-12}$   
 $7.1 \times 10^{-15}$   
 $1.6 \times 10^{-23}$   
 $1.7 \times 10^{-26}$

### Chromates

BaCrO<sub>4</sub>  
PbCrO<sub>4</sub>  
Ag<sub>2</sub>CrO<sub>4</sub>  
SrCrO<sub>4</sub>

$2 \times 10^{-10}$  Ni(OH)<sub>2</sub>  
 $1.8 \times 10^{-14}$  Pd(OH)<sub>2</sub>  
 $1.1 \times 10^{-12}$  Pt(OH)<sub>2</sub>  
 $3.6 \times 10^{-5}$  Ag<sub>2</sub>O(Ag<sup>+</sup>, OH<sup>-</sup>)

$1.6 \times 10^{-14}$   
 $1 \times 10^{-24}$   
 $1 \times 10^{-35}$   
 $2.0 \times 10^{-8}$

*Hydroxides (cont'd)*

	<i>K</i>	<i>Sulfates</i>	
Sr(OH) <sub>2</sub> ·8H <sub>2</sub> O	$3.2 \times 10^{-4}$	BaSO <sub>4</sub>	$9.9 \times 10^{-11}$
Tl(OH)	$7.2 \times 10^{-1}$	CaSO <sub>4</sub> ·2H <sub>2</sub> O	$2.4 \times 10^{-5}$
Tl(OH) <sub>3</sub>	$1 \times 10^{-44}$	PbSO <sub>4</sub>	$1.8 \times 10^{-8}$
Th(OH) <sub>4</sub>	$1 \times 10^{-60}$	Hg <sub>2</sub> SO <sub>4</sub>	$6.2 \times 10^{-7}$
Sn(OH) <sub>2</sub>	$5 \times 10^{-26}$	Ag <sub>2</sub> SO <sub>4</sub>	$1.2 \times 10^{-5}$
Sn(OH) <sub>4</sub>	$1 \times 10^{-66}$	SrSO <sub>4</sub>	$2.8 \times 10^{-7}$
TiO(OH) <sub>2</sub> (TiO <sup>++</sup> , 2OH <sup>-</sup> )	$1 \times 10^{-30}$		
Ti <sub>2</sub> O <sub>3</sub> (Ti <sup>+++</sup> , 3OH <sup>-</sup> )	$1 \times 10^{-40}$	VALUES FOR IONIZATION OF ONE H <sup>+</sup>	
UO <sub>2</sub> (OH) <sub>2</sub> (UO <sub>2</sub> <sup>++</sup> , 2OH <sup>-</sup> )	$2 \times 10^{-15}$		
Zn(OH) <sub>2</sub>	$4.5 \times 10^{-17}$	<i>Acids</i>	

*Iodates*

Ba(IO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	$1.2 \times 10^{-9}$	H <sub>3</sub> AlO <sub>3</sub> (s)	$4 \times 10^{-13}$
Ca(IO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	$1.9 \times 10^{-6}$	HSbO <sub>2</sub>	$10^{-11}$
Cu(IO <sub>3</sub> ) <sub>2</sub>	$1.3 \times 10^{-7}$	HAsO <sub>2</sub>	$6 \times 10^{-10}$
Pb(IO <sub>3</sub> ) <sub>2</sub>	$3.2 \times 10^{-13}$	H <sub>3</sub> AsO <sub>4</sub>	$4.8 \times 10^{-3}$
Hg <sub>2</sub> (IO <sub>3</sub> ) <sub>2</sub>	$1.3 \times 10^{-18}$	H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup>	$10^{-7}$
AgIO <sub>3</sub>	$5.3 \times 10^{-8}$	HAsO <sub>4</sub> <sup>---</sup>	$10^{-13}$
TlIO <sub>3</sub>	$4.5 \times 10^{-6}$	H <sub>3</sub> BO <sub>3</sub>	$5.8 \times 10^{-10}$
		H <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	$10^{-4}$
		HB <sub>4</sub> O <sub>7</sub> <sup>-</sup>	$10^{-9}$

*Iodides*

CuI	$1.1 \times 10^{-12}$	HBrO	$2 \times 10^{-9}$
PbI <sub>2</sub>	$8.7 \times 10^{-9}$	H <sub>2</sub> CO <sub>3</sub>	$4.3 \times 10^{-7}$
Hg <sub>2</sub> I <sub>2</sub>	$4.5 \times 10^{-29}$	HCO <sub>3</sub> <sup>-</sup>	$4.7 \times 10^{-11}$
AgI	$8.5 \times 10^{-17}$	HCO <sub>2</sub> H	$1.8 \times 10^{-4}$
TlI	$5.8 \times 10^{-8}$	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	$5.9 \times 10^{-2}$
		HC <sub>2</sub> O <sub>4</sub> <sup>-</sup>	$6.4 \times 10^{-5}$

*Sulfides*

CdS	$1.4 \times 10^{-28}$	HCN	$1.2 \times 10^{-4}$
Bi <sub>2</sub> S <sub>3</sub>	$1.6 \times 10^{-72}$	HSCN	$10^{-4}$
CoS <sub>α</sub>	$7 \times 10^{-23}$	HClO	$5.6 \times 10^{-8}$
Cu <sub>2</sub> S	$2.5 \times 10^{-50}$	HClO <sub>2</sub>	$10^{-2}$
CuS	$4 \times 10^{-38}$	H <sub>3</sub> CrO <sub>3</sub> (s)	$9 \times 10^{-17}$
FeS	$1 \times 10^{-19}$	HCrO <sub>4</sub> <sup>-</sup>	$3.2 \times 10^{-7}$
PbS	$1.0 \times 10^{-29}$	HF	$7.2 \times 10^{-4}$
MnS	$5.6 \times 10^{-16}$	H <sub>3</sub> GaO <sub>3</sub> (s)	$1 \times 10^{-15}$
Hg <sub>2</sub> S	$1 \times 10^{-46}$	H <sub>2</sub> GeO <sub>3</sub>	$2.6 \times 10^{-9}$
HgS	$3 \times 10^{-63}$	H <sub>5</sub> IO <sub>6</sub>	$2.3 \times 10^{-2}$
NiS <sub>α</sub>	$3 \times 10^{-21}$	H <sub>4</sub> IO <sub>6</sub> <sup>-</sup>	$1 \times 10^{-6}$
PtS	$1 \times 10^{-68}$	HIO	$1 \times 10^{-11}$
Ag <sub>2</sub> S	$1.0 \times 10^{-51}$	H <sub>2</sub> PbO <sub>2</sub> (s)	$2.1 \times 10^{-16}$
Tl <sub>2</sub> S	$1.2 \times 10^{-24}$	HNO <sub>2</sub>	$4.5 \times 10^{-4}$
SnS	$8 \times 10^{-29}$	HN <sub>3</sub>	$1 \times 10^{-4}$
ZnS	$4.5 \times 10^{-24}$	H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	$9 \times 10^{-8}$
		HN <sub>2</sub> O <sub>2</sub> <sup>-</sup>	$1 \times 10^{-11}$
		H <sub>2</sub> OsO <sub>5</sub>	$8 \times 10^{-13}$

*Oxalates*

CaC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	$2.3 \times 10^{-9}$	H <sub>2</sub> O	$1.008 \times 10^{-14}$
Ce <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·10H <sub>2</sub> O	$2.5 \times 10^{-29}$	OH <sup>-</sup>	$< 10^{-36}$
BaC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O	$1.1 \times 10^{-7}$	H <sub>2</sub> O <sub>2</sub>	$2.4 \times 10^{-12}$
MgC <sub>2</sub> O <sub>4</sub>	$8.6 \times 10^{-5}$	H <sub>3</sub> PO <sub>4</sub>	$7.5 \times 10^{-3}$
Hg <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	$1 \times 10^{-13}$	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	$6.2 \times 10^{-8}$
Ag <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	$1.1 \times 10^{-11}$	HPO <sub>4</sub> <sup>---</sup>	$10^{-12}$
SrC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	$5.6 \times 10^{-8}$	H <sub>3</sub> PO <sub>3</sub>	$1.6 \times 10^{-2}$

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<i>Acids (cont'd)</i>		$\text{H}_2\text{SO}_3$	$1.2 \times 10^{-2}$
$\text{H}_2\text{PO}_3^-$	$7 \times 10^{-7}$	$\text{HSO}_3^-$	$1 \times 10^{-7}$
$\text{H}_3\text{PO}_2$	$1 \times 10^{-2}$	$\text{HSO}_4^-$	$1.2 \times 10^{-2}$
$\text{H}_2\text{Se}$	$1.7 \times 10^{-4}$	$\text{H}_2\text{Te}$	$2.3 \times 10^{-3}$
$\text{HSe}^-$	$1 \times 10^{-10}$	$\text{HTe}^-$	$1 \times 10^{-5}$
$\text{HSeO}_4^-$	$1 \times 10^{-2}$	$\text{H}_2\text{TeO}_3$	$2 \times 10^{-3}$
$\text{H}_3\text{SiO}_3$	$1 \times 10^{-10}$	$\text{H}_2\text{SnO}_2(\text{s})$	$6 \times 10^{-18}$
$\text{H}_2\text{S}$	$1.1 \times 10^{-7}$	$\text{H}_2\text{ZrO}_3$	$10^{-18}$
$\text{HS}^-$	$1.0 \times 10^{-13}$		

# Appendix XII

## BUFFER SOLUTIONS

The following solutions may be employed to maintain desired concentrations of  $H^+$  or  $OH^-$ . These concentrations are expressed as  $pH = \log_{10} 1/(H^+)$  e.g.,  $0.01N H^+$  has a  $pH$  of 2.

### SORENSEN'S PHOSPHATE SOLUTIONS

$KH_2PO_4$ , 9.078 g. per liter, and  $Na_2HPO_4 \cdot 2H_2O$ , 11.876 g. per liter

$Na_2HPO_4$ (cc.) ...	0.25	0.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	9.5
$KH_2PO_4$ (cc.) ....	9.75	9.5	9.0	8.0	7.0	6.0	5.0	4.0	3.0	2.0	1.0	0.5
pH.....	5.29	5.59	5.91	6.24	6.47	6.64	6.81	6.98	7.17	7.38	7.73	8.04

### ACETIC ACID-ACETATE SOLUTIONS, BY WALPOLE-CLARK

$CH_3COOH$ m per l	0.185	0.176	0.164	0.147	0.126	0.102	0.080	0.059	0.042	0.019
$CH_3COONa$ m per l	0.015	0.024	0.036	0.053	0.074	0.098	0.120	0.1	0.158	0.181
pH.....	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.6

### CLARK AND LUBS, BORATE SOLUTIONS

X cc. of 0.2M NaOH added to 50 cc. of a mixture of 0.2M $H_3BO_3$ + 0.2M KCl and diluted to 200 cc.	cc.	2.61	3.97	5.90	8.50	12.00	16.30	21.30	26.70	32.00	36.85	40.80	43.90
	pH	7.8	8.0	8.2	8.4	8.6	8.8	9.0	9.2	9.4	9.6	9.8	10.0

# Appendix XIII

## INDICATORS

CLARK AND LUBS' LIST, COVERING RANGE FROM STRONG ACID TO STRONG BASE

Abbreviations: c, colorless; r, red; y, yellow; b, blue; pu, purple; o, orange; v, violet.

INDICATOR	USEFUL RANGE $\text{pH} = \log_{10} \frac{1}{(\text{H}^+)}$
Thymol blue	r 1.2-2.8 y
Bromphenol blue	y 3.0-4.6 b
Bromcresol green	y 3.8-5.4 b
Methyl red	r 4.2-6.3 y
Chlorphenol red	y 5.0-6.6 r
Bromcresol purple	y 5.2-6.8 pu
Bromthymol blue	y 6.0-7.6 b
Phenol red	y 6.8-8.4 r
Cresol red	y 7.2-8.8 r
Metacresol purple	y 7.6-9.2 pu
Thymol blue	y 8.0-9.6 b
O-cresolphthalein	c 8.2-9.8 r

## INDICATORS IN COMMON USE

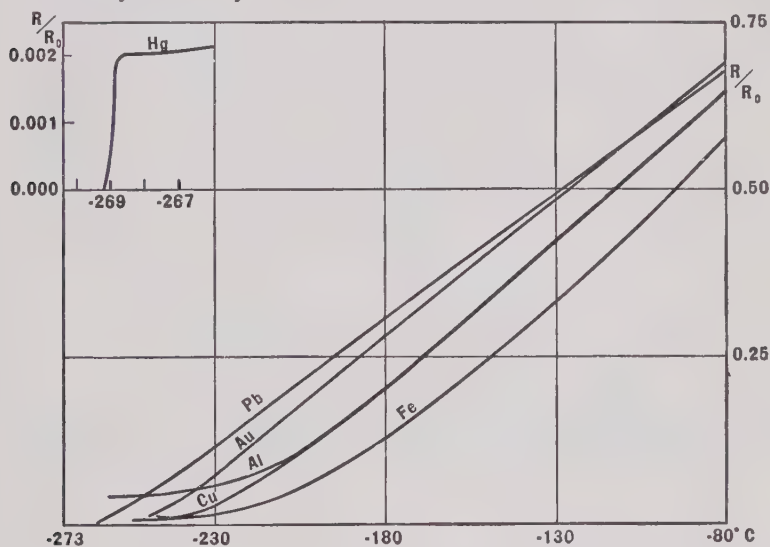
INDICATOR	pH RANGE
Methyl orange	r 3.1 — 4.4 y
Resorcin blue	r 4.4 — 6.2 b
Litmus	r 4.5 — 8.3 b
Phenolphthalein	c 8.3 — 10.0 r
Methyl violet	y 0.15 — 3.2 v
Trinitrobenzene	c 12.0 — 14.0 o



# Appendix XIV

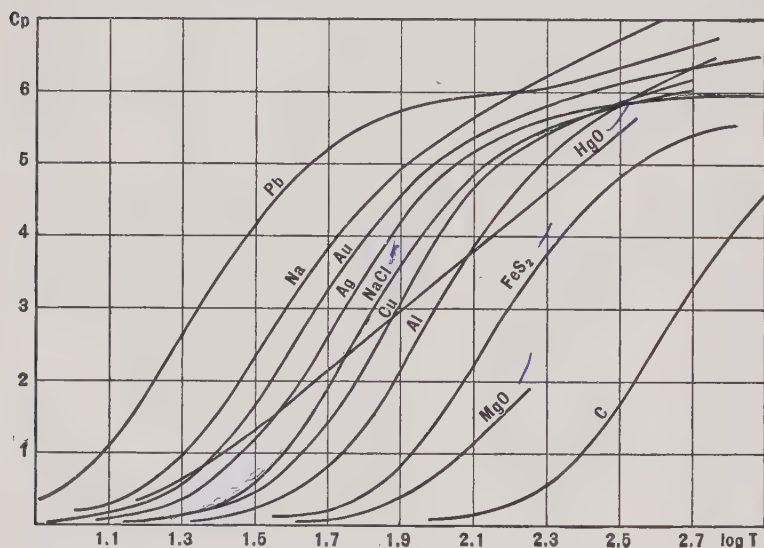
## CHANGE OF RESISTANCE OF METALS WITH TEMPERATURE

$R/R_0$  is the ratio of the resistance to the value at  $0^\circ\text{C}$ . Insert shows supraconductivity of mercury.



# Appendix XV

## SPECIFIC HEAT OF METALS AND COMPOUNDS AT LOW TEMPERATURES



# Appendix XVI

## COVALENT BOND ENERGIES AND ATOMIC RADII

Values from Pauling. *Nature of Chemical Bond*. Cornell University Press, 1939

### COVALENT BOND ENERGIES

BOND	ENERGY KCAL./MOLE	BOND	ENERGY KCAL./MOLE	BOND	ENERGY KCAL./MOLE
H—H	103.4	H—Cl	102.7	As—Cl	60.3
C—C	58.6	H—Br	87.3	As—Br	48.0
Si—Si	42.5	H—I	71.4	As—I	33.1
Ge—Ge	42.5	C—Si	57.6	O—F	58.6
N—N	23.6	C—N	48.6	O—Cl	49.3
P—P	18.9	C—O	70.0	S—Cl	66.1
As—As	15.1	C—S	54.5	S—B	57.2
O—O	34.9	C—F	107.0	Se—Cl	66.8
S—S	63.8	C—Cl	66.5	Cl—F	86.4
Se—Se	57.6	C—Br	54.0	Br—Cl	52.7
F—F	63.5	C—I	45.5	I—Cl	51.0
Cl—Cl	57.8	Si—O	89.3	I—Br	42.9
Br—Br	46.1	Si—S	60.9	C=C	100
I—I	36.2	Si—F	143.0	C≡C	123
C—H	87.3	Si—Cl	85.8	C=O	142 formaldehyde
Si—H	75.1	Si—Br	69.3	C=O	152 ketones
N—H	83.7	Si—I	51.1	C=N	94
P—H	63.0	Ge—Cl	104.1	C≡N	150 cyanides
As—H	47.3	N—F	68.8	C=S	103
O—H	110.2	N—Cl	38.4	O=O	96 'Δ O <sub>2</sub>
S—H	87.5	P—Cl	62.8	N≡N	170 normal N <sub>2</sub>
Se—H	73.0	P—Br	49.2		
H—F	147.5	P—I	35.2		

## TETRAHEDRAL COVALENT RADII

ELEMENT	RADIUS IN Å	ELEMENT	RADIUS IN Å
Be	1.06	As	1.18
B	0.88	Se	1.14
C	0.77	Br	1.11
N	0.70	Ag	1.53
O	0.66	Cd	1.48
F	0.64	In	1.44
Mg	1.40	Sn	1.40
Al	1.26	Sb	1.36
Si	1.17	Te	1.32
P	1.10	I	1.28
S	1.04	Au	1.50
Cl	0.99	Hg	1.48
Cu	1.35	Tl	1.47
Zn	1.31	Pt	1.46
Ga	1.26	Bi	1.46
Ge	1.22		

## OCTAHEDRAL RADII

ELEMENT	RADIUS IN Å	ELEMENT	RADIUS IN Å
Fe <sup>2</sup>	1.23	Ir <sup>3</sup>	1.32
Co <sup>2</sup>	1.32	Pt <sup>4</sup>	1.31
Co <sup>3</sup>	1.22	Ti <sup>4</sup>	1.36
Ni <sup>2</sup>	1.39	Zn <sup>4</sup>	1.48
Ru <sup>2</sup>	1.33	Sn <sup>4</sup>	1.45
Rh <sup>3</sup>	1.32	Pb <sup>4</sup>	1.50
Pd <sup>4</sup>	1.31	Se <sup>4</sup>	1.40
As <sup>2</sup>	1.33		

# Appendix XVII

## TABLE OF CONVERSION FACTORS

Values in agreement with International Critical Tables

### *Length and volume*

1 Meter = 39.37 in. = (100/2.54) in.	
1 Yard (U.S.) = 91.44018 cm.	log = 1.9611371
1 Yard (British) = 91.43992 cm.	log = 1.9611350
1 Liter = 1000.027 cm. <sup>3</sup>	log = 3.0000117
1 Cubic foot (U.S.) = 28317.0 cm. <sup>3</sup>	log = 4.4520474
1 Gallon (U.S.) = 3785.4 cm. <sup>3</sup>	log = 3.5781157
1 Gallon (British) = 4546.1 cm. <sup>3</sup>	log = 3.6576376
1 Quart, dry (U.S.) = 1101-23 cm. <sup>3</sup>	log = 3.0418770
1 Quart, liquid (U.S.) = 946.358 cm. <sup>3</sup>	log = 2.9760557
1 Fluid ounce (U.S.) = 29.5737 cm. <sup>3</sup>	log = 1.4709057

### *Weight*

1 Grain = 64.799 mg.	log = 1.8115677
1 Ounce (avoirdupois) = 28.350 g.	log = 1.4525458
1 Pound (avoirdupois) = 453.59243 g. = 1000/2.2046223	log = 2.6566658
1 Ton, short (2000 pounds) = 907.185 kg.	log = 2.9576958
1 Ton, long (2240 pounds) = 1016.047 kg.	log = 3.0069138

### *Pressure*

1 Pound weight per sq. in. (U.S.) = 68947.3 dynes cm. <sup>-2</sup>	log = 4.8385173
1 Centimeter of water at 4° C. = 980.638 dynes cm. <sup>-2</sup>	log = 2.9915090
1 Inch of water at 4° C. (U.S.) = 2490.827 dynes cm. <sup>-2</sup>	log = 3.3963436
1 Centimeter of mercury at 0° C. = 13332.24 dynes cm. <sup>-2</sup>	log = 4.1249031
1 Inch of mercury at 0° C. (U.S.) = 33863.95 dynes cm. <sup>-2</sup>	log = 4.5297377

### *Density*

1 Gram per milliliter = specific gravity, t°/4° = 0.999973 g. cm. <sup>-3</sup>	log = 1.9999883
1 Pound per cu. in. (U.S.) = 27.67974 g. cm. <sup>-3</sup>	log = 1.4221621
1 Pound per cu. ft. (U.S.) = 0.016018 g. cm. <sup>-3</sup>	log = 2.2046183
1 Pound per gal. (U.S.) = 0.1198257 g. cm. <sup>-3</sup>	log = 1.0785502

### *Energy*

1 Cubic centimeter-atmosphere 0.10133 = 0.101325 joules (absolute)	log = 1.0057167
1 Gram calorie (15°) = 4.185 joules absolute	log = 0.6216955
1 British Thermal Unit (39° F.) = 1060.4 joules (abs.)	log = 3.0254697
1 British Thermal Unit (mean) = 1054.8 joules (abs.)	log = 3.0231701
1 British Thermal Unit (60° F.) = 1054.6 joules (abs.)	log = 3.0230878

*Work*

1 Watt (International) = 1.00032 watt (absolute)	log = 0.0001390
1 Kilogram-meter per sec. = 9.80665 watt (abs.)	log = 0.9915207
1 Foot-pound per sec. (U.S.) = 1.355821 watt (abs.)	log = 0.1322022
1 Horsepower (U.S., British) = 746.00 watt (abs.)	log = 2.8727388
1 Horsepower (Continental Europe) = 736.00 watt (abs.)	log = 2.8660778
1 Cheval-vapeur (75 kg.-m. per sec.) = 735.499 watt (abs.)	log = 2.8665820

*Temperature*

Fahrenheit  $x^{\circ}$  F. =  $(5/9)(x - 32)^{\circ}$  C.

Reaumur  $x^{\circ}$  R. =  $(5/4)x^{\circ}$  C.



# Appendix XVIII

## THE ELECTRON STRUCTURE OF THE ELEMENTS

ATOMIC NUMBER	ELEMENT	NUMBER OF ELECTRONS IN EACH QUANTUM GROUP																			
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	5g	6s	6p	6d	7s	7p
1	H	1																			
2	He	2																			
3	Li	2	1																		
4	Be	2	2																		
5	B	2	2	1																	
6	C	2	2	2																	
7	N	2	2	3																	
8	O	2	2	4																	
9	F	2	2	5																	
10	Ne	2	2	6																	
11	Na	2	2	6	1																
12	Mg	2	2	6	2																
13	Al	2	2	6	2	1															
14	Si	2	2	6	2	2															
15	P	2	2	6	2	3															
16	S	2	2	6	2	4															
17	Cl	2	2	6	2	5															
18	A	2	2	6	2	6															
19	K	2	2	6	2	6		1													
20	Ca	2	2	6	2	6		2													
21	Sc	2	2	6	2	6	1	2													
22	Ti	2	2	6	2	6	2	2													
23	V	2	2	6	2	6	3	2													
24	Cr	2	2	6	2	6	5	1													
25	Mn	2	2	6	2	6	5	2													
26	Fe	2	2	6	2	6	6	2													
27	Co	2	2	6	2	6	7	2													
28	Ni	2	2	6	2	6	8	2													
29	Cu	2	2	6	2	6	10	1													
30	Zn	2	2	6	2	6	10	2													
31	Ga	2	2	6	2	6	10	2	1												
32	Ge	2	2	6	2	6	10	2	2												
33	As	2	2	6	2	6	10	2	3												

ATOMIC NUMBER	ELEMENT	NUMBER OF ELECTRONS IN EACH QUANTUM GROUP															
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	5g	6s
34	Se	2	2	6	2	6	10	2	4								
35	Br	2	2	6	2	6	10	2	5								
36	Kr	2	2	6	2	6	10	2	6								
37	Rb	2	2	6	2	6	10	2	6			1					
38	Sr	2	2	6	2	6	10	2	6			2					
39	Y	2	2	6	2	6	10	2	6	1		2					
40	Zr	2	2	6	2	6	10	2	6	2		2					
41	Cb	2	2	6	2	6	10	2	6	4		1					
42	Mo	2	2	6	2	6	10	2	6	5		1					
43	Ma	2	2	6	2	6	10	2	6	6		1					
44	Ru	2	2	6	2	6	10	2	6	7		1					
45	Rh	2	2	6	2	6	10	2	6	8		1					
46	Pd	2	2	6	2	6	10	2	6	10							
47	Ag	2	2	6	2	6	10	2	6	10		1					
48	Cd	2	2	6	2	6	10	2	6	10		2					
49	In	2	2	6	2	6	10	2	6	10		2	1				
50	Sn	2	2	6	2	6	10	2	6	10		2	2				
51	Sb	2	2	6	2	6	10	2	6	10		2	3				
52	Te	2	2	6	2	6	10	2	6	10		2	4				
53	I	2	2	6	2	6	10	2	6	10		2	5				
54	Xe	2	2	6	2	6	10	2	6	10		2	6				
55	Cs	2	2	6	2	6	10	2	6	10		2	6			1	
56	Ba	2	2	6	2	6	10	2	6	10		2	6			2	
57	La	2	2	6	2	6	10	2	6	10		2	6	1		2	
58	Ce	2	2	6	2	6	10	2	6	10	1	2	6	1		2	
59	Pr	2	2	6	2	6	10	2	6	10	2	2	6	1		2	
60	Nd	2	2	6	2	6	10	2	6	10	3	2	6	1		2	
61	Il	2	2	6	2	6	10	2	6	10	4	2	6	1		2	
62	Sm	2	2	6	2	6	10	2	6	10	5	2	6	1		2	
63	Eu	2	2	6	2	6	10	2	6	10	6	2	6	1		2	
64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2	
65	Tb	2	2	6	2	6	10	2	6	10	8	2	6	1		2	
66	Dy	2	2	6	2	6	10	2	6	10	9	2	6	1		2	
67	Ho	2	2	6	2	6	10	2	6	10	10	2	6	1		2	
68	Er	2	2	6	2	6	10	2	6	10	11	2	6	1		2	
69	Tu	2	2	6	2	6	10	2	6	10	12	2	6	1		2	
70	Yb	2	2	6	2	6	10	2	6	10	13	2	6	1		2	
71	Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2	
72	Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2	
73	Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2	
74	W	2	2	6	2	6	10	2	6	10	14	2	6	4		2	
75	Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2	
76	Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2	
77	Ir	2	2	6	2	6	10	2	6	10	14	2	6	9			
78	Pt	2	2	6	2	6	10	2	6	10	14	2	6	9		1	
79	Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1	

ATOMIC NUMBER	ELEMENT	NUMBER OF ELECTRONS IN EACH QUANTUM GROUP																			
		1 <sub>s</sub>	2 <sub>s</sub>	2 <sub>p</sub>	3 <sub>s</sub>	3 <sub>p</sub>	3 <sub>d</sub>	4 <sub>s</sub>	4 <sub>p</sub>	4 <sub>d</sub>	4 <sub>f</sub>	5 <sub>s</sub>	5 <sub>p</sub>	5 <sub>d</sub>	5 <sub>f</sub>	5 <sub>g</sub>	6 <sub>s</sub>	6 <sub>p</sub>	6 <sub>d</sub>	7 <sub>s</sub>	7 <sub>p</sub>
80	Hg	2	2	6	2	6	10	2	6	10	14	2	6	10			2				
81	Tl	2	2	6	2	6	10	2	6	10	14	2	6	10			2	1			
82	Pb	2	2	6	2	6	10	2	6	10	14	2	6	10			2	2			
83	Bi	2	2	6	2	6	10	2	6	10	14	2	6	10			2	3			
84	Po	2	2	6	2	6	10	2	6	10	14	2	6	10			2	4			
85	—	2	2	6	2	6	10	2	6	10	14	2	6	10			2	5			
86	Rn	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6			
87	—	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6		1	
88	Ra	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6		2	
89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	1	2	
90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	2	2	
91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	3	2	
92	U	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	4	2	

# Appendix XIX

## TABLE OF DENSITIES, MELTING POINTS, BOILING POINTS, COLORS, AND SOLUBILITIES OF INORGANIC COMPOUNDS

Values for densities are in grams per cc. Temperatures 15–25° C. Values for solubilities are in grams of anhydrous salt per 100 grams of water solution.

Abbreviations for colors: bk, black; bl, blue; br, brown; c, colorless or white if finely divided; d, dark; gr, green; gy, grey; l, light; or, orange; pk, pink; pu, purple; r, red; ro, rose; sil, silver; v, violet; w, white; y, yellow.

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
<i>Aluminum</i>					
Al	2.71	658.6	2057	gy-w	sol. H <sup>+</sup> and OH <sup>-</sup>
Al <sub>2</sub> O <sub>3</sub>	4.00	2045	2977	c	v. sl. sol.
Al <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	3.41	d. 360		c	0.0001(20°)
Al(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>3</sub>		d.		c	sol. but hydr.
Al(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> OH				c	sl. sol.
Al(BrO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O		62.3		c	sol.
AlBr <sub>3</sub>	3.01	97.5	265	c	sol.
Al <sub>4</sub> C <sub>3</sub>	2.36	high		y	giv. Al(OH) <sub>3</sub> + CH <sub>4</sub>
Al(ClO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O		d.		c	v. sol.
AlCl <sub>3</sub>	2.44	190 (2½ at.)	180.2	c	6 aq. 41.41(15°)
AlF <sub>3</sub>	3.07	1040		c	sl. sol.
Al(OH) <sub>3</sub>	2.4	d.		c	v. sl. sol.
AlI <sub>3</sub>	3.98	191	385.5	br	6 aq. v. sol.
Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O		73	d. 134	c	4 aq. 38.9(25°)
AlN		2150		gy	not sol.
AlPO <sub>4</sub>	2.59	high		c	v. sl. sol.
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2.7	d. 770		c	18 aq. 26.6(20°)
AlNH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	1.64	93		c	6.2(20°), 26.0(80°)
Al <sub>2</sub> S <sub>3</sub>	2.02	1100	sub. 1550	y	hydr.
AlTi(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	2.32	91		c	5.1(15°)
AlK(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	1.76	92		c	4.8(15°), 60.6(100°)
Al <sub>2</sub> O <sub>3</sub> ·Si <sub>2</sub> O <sub>4</sub>	3.15	d. 1810		c	v. sl. sol.
<i>Ammonia</i>					
NH <sub>3</sub>	0.82(79°)	— 77.6	— 33.4	c	47.5(0°), 6.9(100°)
NH <sub>4</sub> OH		— 79	d.	c	cf. NH <sub>3</sub>
(NH <sub>4</sub> ) <sub>2</sub> O		— 79	d.	c	
NH <sub>4</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> (acetate)	1.07	114.0		c	60(40°)
NH <sub>4</sub> H <sub>2</sub> AsO <sub>4</sub>	2.31			c	sol.
NH <sub>4</sub> AsO <sub>2</sub>				c	v. sol.
NH <sub>4</sub> Br	2.33		sub. 542	c	41.1(15°), 56.1(100°)

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O		d.		c	50(15°)
NH <sub>4</sub> HCO <sub>3</sub>	1.59			c	21(30°)
NH <sub>4</sub> Cl	1.54	d. 350		c	22.9(0°), 29.3(30°)
NH <sub>4</sub> ClO <sub>4</sub>	1.95	d.		c	20.8(20°), 57(100°)
(NH <sub>4</sub> ) <sub>2</sub> CrO <sub>4</sub>	1.8	d. 180		y	28(30°)
NH <sub>4</sub> CNO		d.		c	sol.
NH <sub>4</sub> CN		d. 36		c	sol.
(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	2.15	d.		r-br	32(30°)
NH <sub>4</sub> F		d.		c	v. sol.
NH <sub>4</sub> I	2.56	d.	sub. 551	c	67(25°)
NH <sub>4</sub> IO <sub>3</sub>	3.31	d. 150		c	2.5(0°), 12.6(100°)
NH <sub>4</sub> MgAsO <sub>4</sub> ·6H <sub>2</sub> O	1.93	d.		c	0.038(20°)
NH <sub>4</sub> MgPO <sub>4</sub> ·6H <sub>2</sub> O	1.65	d.		c	0.024(15°)
(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O		d.		c	sol.
NH <sub>4</sub> NO <sub>3</sub>	α1.66 β1.72	169.6	d. 210 d. 210		70(30°)
NH <sub>4</sub> NO <sub>2</sub>	1.69	d.		c	sol.
(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	1.50			c	4.2(20°), 9.3(50°)
NH <sub>4</sub> MnO <sub>4</sub>	2.21	d. 60		g	8(15°)
(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	1.98	d. 120		c	34(0°)
(NH <sub>4</sub> ) <sub>2</sub> PtCl <sub>6</sub>	3.06	d.		y	0.67(20°), 1.25(100°)
(NH <sub>4</sub> ) <sub>2</sub> PtCl <sub>4</sub>		d.		y	sol.
(NH <sub>4</sub> ) <sub>2</sub> PdCl <sub>6</sub>	2.42	d.		r	sl. sol.
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	1.62	d.		c	v. sol.
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	1.803			c	18.0(50°)
(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> ·12MoO <sub>3</sub> ·3H <sub>2</sub> O		d.		y	0.03(15°)
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1.77	d.		c	41.4(0°), 43.8(30°)
(NH <sub>4</sub> ) <sub>2</sub> S		d.		y	v. sol. giv. HS <sup>-</sup>
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>3</sub> ·H <sub>2</sub> O		d.		c	v. sol.
(NH <sub>4</sub> ) <sub>2</sub> Se			d.	br	sol.
NH <sub>4</sub> CNS	1.31(13°)	146	d. 170	c	55(0°), 62(20°)
(NH <sub>4</sub> ) <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>8</sub>	1.60	d.		c	5.9(15°)
<i>Antimony</i>					
Sb	6.68	630	1440	gr	not sol.
HSb(OH) <sub>6</sub>	6.6	d.		c	sl. sol.
H <sub>3</sub> SbO <sub>3</sub>		d.		c	v. sl. sol.
Sb <sub>2</sub> O <sub>3</sub>	5.67	655	1425	c	0.002(15°)
Sb <sub>2</sub> O <sub>4</sub>	4.07	1060		c	v. sl. sol.
Sb <sub>2</sub> O <sub>5</sub>	3.78	450	1060	y	v. sl. sol.
SbBr <sub>3</sub>	4.15	96.6	280	y	sol. hydr.
SbCl <sub>3</sub>	3.14	73.4	219	c	910 g./100 g. H <sub>2</sub> O at 20°
SbCl <sub>5</sub>	2.34	4.0	92 at 30 mm.	y	hydr.
SbF <sub>3</sub>	4.38	292		c	83(25°)
SbF <sub>5</sub>	2.99	7	149.5	c	hydr.
SbH <sub>3</sub>	1.226	- 88	- 18	c	0.12 (1 atm.p.)
SbI <sub>3</sub> Trig	4.85	167	401	y	hydr.
SbI <sub>5</sub>		79		br	
SbOCl		d. 170		c	v. sl. sol.
Sb <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	3.63	d.		c	hydr.
Sb <sub>2</sub> S <sub>3</sub>	4.64	546		bk, r	0.000175
Sb <sub>2</sub> S <sub>5</sub>	4.12			or	v. sl. sol.
Sb <sub>2</sub> Se <sub>3</sub>		611		gy	v. sl. sol.
Sb <sub>2</sub> Te <sub>3</sub>		629		gy	
(SbO)KC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·½H <sub>2</sub> O	2.61	½ aq. 100		c	7.0(25°)
<i>Argon</i>					
A	1.140	- 189.3	- 185.8	c	5, 6 cc.(0°)
<i>Arsenic</i>					
As	5.7	817 (36 atm.)	610	sil	not sol.

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
$\text{H}_3\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	2-2.5	35.5	1 aq, 160	c	sol.
$\text{H}_4\text{As}_2\text{O}_7$		206 d.		c	sol.
$\text{As}_2\text{O}_3$	3.7	218 sub.		c	2.04(25°)
$\text{As}_2\text{O}_5$	4.15	315		c	cf. $\text{H}_3\text{AsO}_4$
$\text{AsBr}_3$	3.54	31	221	y	sol.
$\text{AsCl}_3$	1.2.16	- 16.1	122.0	c	sol.
$\text{AsCl}_5$		- 40		c	hydr.
$\text{AsF}_3$	1.2.66	- 8.5		c	hydr.
$\text{AsF}_5$		- 88.7	- 58.2	c	hydr.
$\text{AsH}_3$		- 113.5	- 55	c	sl. sol.
$\text{AsI}_3$	4.39	146	403	or-r	6(25°)
$\text{AsOCl}$				br	sol.
$\text{As}_2\text{S}_2 \alpha, \beta$	$\alpha$ 3.51 $\beta$ 3.25	$\beta$ 307	565	r	v. sl. sol.
$\text{As}_2\text{S}_3$	3.43	300	700	r & y	0.00005
$\text{As}_2\text{S}_5$		sub.		y	v. sl. sol.
<i>Barium</i>					
Ba	3.78	850	1640	y-w	giv. $\text{Ba}(\text{OH})_2 + \text{H}_2$
BaO	5.72	1923		c	8 aq. 3.36(20°), 47.6(80°)
$\text{BaO}_2$	4.96	d.		gy	v. sl. sol.
$\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$	2.19	d.		c	43.3(26°)
$\text{BaHAsO}_4 \cdot \text{H}_2\text{O}$	3.93	d.		c	sl. sol.
$\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$	3.99			c	0.3(0°), 5.67(100°)
$\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$	3.69	an. 847		c	60(20°)
$\text{BaCO}_3 \alpha, \beta$	$\alpha$ 4.43	$\beta$ 1740(90 atm.)	d.	c	0.002(20°), 0.006(100°)
$\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$	3.18	d. 120		c	21.5(25°), 33.9(100°)
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	3.10	an. 960		c	26.3(20°), 37.0(100°)
$\text{BaCrO}_4$	4.98			y	0.00038(20°)
$\text{BaF}_2$	4.83	1287	1400	c	0.16(18°)
$\text{BaH}_2$	4.21	d. 675		c	giv. $\text{Ba}(\text{OH})_2 + \text{H}_2$
$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	2.13	77.9		c	cf. BaO
$\text{Ba}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$	5.5	aq. 130		c	0.028(20°), 0.20(100°)
$\text{BaI}_2$	5.15	d. 740		c	6 aq. 66.5(20°)
$\text{Ba}(\text{NO}_3)_2$	3.24	585	d.	c	1 aq. 38.6(20°)
$\text{BaC}_2\text{O}_4$	2.66	d.		c	2 aq. 0.0024(25°)
$\text{Ba}(\text{ClO}_4)_2$		505		c	66.5(25°)
$\text{Ba}(\text{MnO}_4)_2$	3.77	d.		gr	62.5(11°), 75.4(25°)
$\text{BaMoO}_4$	4.65			c	0.0058(23°)
$\text{Ba}_3(\text{PO}_4)_2$	4.11	1727		c	v. sl. sol.
$\text{BaH}_4(\text{PO}_4)_2$	2.90			c	sol.
$\text{BaHPO}_4$	4.16			c	0.01(20°)
$\text{Ba}_2\text{P}_2\text{O}_7$	4.11			c	0.01
$\text{BaSO}_4$	4.50	1350		c	0.00024(20°)
$\text{BaSO}_3$			d.	c	0.02(20°)
BaS	4.25	high		gy-gr	hydr.
<i>Beryllium</i>					
Be	1.73	1350	1500	gr-w	0.36(0°)
BeO	3.03	2400	3900	c	$2 \times 10^{-5}(20^\circ)$
$\text{Be}(\text{OH})_2$		d.		w	hot. sol.
$\text{BeBr}_2$		490	474	c	sol.
$\text{BeCO}_3 \cdot 4\text{H}_2\text{O}$		d. 100		c	0.36(0°)
$\text{BeCl}_2$	1.90	405	487	c	v. sol.
$\text{BeF}_2$	2.1	ca. 800		c	giv. oxy-salt
$\text{BeI}_2$	4.20	510	sub.	c	sol.
$\text{Be}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$		60		c	sol.
$\text{BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$				c	40 g./100 g. $\text{H}_2\text{O}$ at 25°
$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$	1.71	2 aq. 100	d.	c	29.8(25°)
<i>Bismuth</i>					
Bi	9.80	271	1420	gy-w	not sol.
$\text{HBiO}_3$	5.75	d. 120		r	evol. $\text{O}_2$
$\text{Bi}_2\text{O}_3$	8.9	817	1900	y	v. sl. sol.



FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
$\text{Bi}_2\text{O}_3$	5.10	d. 150		r	v. sl. sol.
$\text{Bi}(\text{OH})_3$	4.36	d. 100		c	0.00014
$\text{BiBr}_3$	5.7	218	460.8	y	hydr.
$\text{Bi}_2\text{O}_3\cdot\text{CO}_2\cdot\text{H}_2\text{O}$	6.86	d.		c	v. sl. sol.
$\text{BiCl}_2$				v	d.
$\text{BiCl}_3$	4.7	224	441	c	hydr. sol. in $\text{HCl}$
$\text{BiOCl}$	7.72	high		c	v. sl. sol.
$\text{BiOF}$	7.5			c	v. sl. sol.
$\text{BiI}_3$	5.7	439	d. 500	gy-bl	hydr.
$\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$	2.83	d. 30		c	v. sol. in dil. $\text{HNO}_3$
$\text{BiONO}_3\cdot\text{H}_2\text{O}$	4.93	d. 260		c	v. sl. sol.
$\text{BiPO}_4$	6.32	d.		c	v. sl. sol.
$\text{Bi}_2\text{S}_3$	7.39	747		br	0.000018(18°)
$\text{Bi}_2(\text{SO}_4)_3$	5.1	d. 418		c	hydr. sol. in $\text{H}_2\text{SO}_4$
<i>Boron</i>					
$\text{B}$	2.45	2300	2550	br	not sol.
$\text{H}_3\text{BO}_3$	1.43	185		c	4.8(20°), 28.7(100°)
$\text{B}_2\text{O}_3$	1.85	577		c	cf. $\text{H}_3\text{BO}_3$
$\text{BBr}_3$	1.2.60	— 45	91.0		hydr.
$\text{B}_2\text{C}$	2.6	2350		bk	not sol.
$\text{BCl}_3$	1.1.43	— 107	12.5	c	hydr.
$\text{BF}_3$		— 128	— 101.9	c	1.06 cc/cc $\text{H}_2\text{O}$ at 0°, 1 atm.
$\text{B}_2\text{H}_6$		— 169	— 92.4	c	sl. sol.
$\text{B}_4\text{H}_{10}$		— 112	16	c	sl. sol.
$\text{B}_{10}\text{H}_{14}$	0.94	99.5		c	sl. sol.
$\text{BI}_3$	1.3.35	43	210	c	hydr.
$\text{B}_2\text{S}_3$	1.55	310		c	hydr.
<i>Bromine</i>					
$\text{Br}_2$	3.4	— 7.2	58.78	br	4.0(0°), 3.3(25°)
$\text{HBrO}_3$		d. 100		l-y	v. sol.
$\text{BrCl}\cdot 10\text{H}_2\text{O}$		d. 7		y	v. sol. hydr.
$\text{BrF}_3$		5	135	y	hydr.
<i>Cadmium</i>					
$\text{Cd}$	8.6	320.9	765	sil	v. sl. sol.
$\text{CdO}$	8.15		1559	br	cf. $\text{Cd}(\text{OH})_2\cdot\text{Sol. H}^+$
$\text{Cd}(\text{OH})_2$	4.79	3.300		c	0.00026(25°)
$\text{Cd}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot 3\text{H}_2\text{O}$	2.01			c	v. sol.
$\text{CdBr}_2$	5.19	583	963	y	4 aq. 48.8(18°)
$\text{CdCO}_3$	4.26	d. < 500		c	v. sl. sol.
$\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$	3.32	an. 568	967	c	56.3(30°)
$\text{CdF}_2$	6.64	1110		c	4.3(25°)
$\text{CdI}_2 \alpha$	$\alpha$ 5.67	$\alpha$ 388	$\alpha$ 796	br	$\alpha$ 46.0(18°)
$\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$	2.45	59.4	132	c	58.4(30°)
$\text{CdC}_2\text{O}_4$	3.32	d. 340		c	0.0033(18°)
$\text{Cd}_3(\text{PO}_4)_2$		1500		c	v. sl. sol.
$\text{CdSiO}_3$	4.93	1242		c	v. sl. sol.
$3\text{CdSO}_4\cdot 8\text{H}_2\text{O}$	3.09			c	43.4(26°), 1 aq. 60.8(100°)
$\text{CdSO}_4$	4.69	1000		c	
$\text{CdS}$	4.66	1750(100 atm.)		y	0.00013(18°)
<i>Calcium</i>					
$\text{Ca}$	1.55	851	1487	sil	$\text{Ca}(\text{OH})_2 + \text{H}_2$
$\text{CaO}$	3.32	2707		c	cf. $\text{Ca}(\text{OH})_2$
$\text{Ca}(\text{OH})_2$	2.34	d. 580		c	0.165(20°), 0.08(100°)
$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot \text{H}_2\text{O}$		d.		gy	25.8(20°), 22.9(100°)
$\text{CaBr}_2$	3.35	730	810	c	6 aq. 58.8(20°)
$\text{CaC}_2$	2.22	2300		gy	giv. $\text{Ca}(\text{OH})_2 + \text{C}_2\text{H}_2$
$\text{CaCO}_3$ (Aragonite)	2.93		d.	c	0.00153(25°)
$\text{CaCO}_3$ (Calcite)	2.71	1282	d.	c	0.00143(25°)
$\text{CaCl}_2$	2.15	772		c	cf. 6 aq.
$\text{CaCl}_2\cdot 6\text{H}_2\text{O}$	1.68	29.92		c	42.7(20°), 2 aq. 61.4(100°)

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
CaCrO <sub>4</sub>			d.	y	2 aq. 14(20°)
CaF <sub>2</sub>	3.18	1392		c	0.0016(18°)
CaH <sub>2</sub>	1.7	d. 675		c	giv. Ca(OH) <sub>2</sub> + H <sub>2</sub>
Ca(ClO) <sub>3</sub> ·4H <sub>2</sub> O		d.		c	v. sol.
CaI <sub>2</sub>	3.96	575	718	y-w	6 aq. 67(20°)
Ca <sub>2</sub> N <sub>3</sub>	2.63	900		l-br	hydr. slowly
Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O α, β	α1.82	α42.7	132	c	54.8(18°)
CaC <sub>2</sub> O <sub>4</sub>	2.2	d.		c	0.0006(18°), 0.0014(95°)
Ca(MnO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	2.4	d.		pu	v. sol.
Ca <sub>3</sub> P <sub>2</sub>	2.51	> 1600		r	giv. PH <sub>3</sub>
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	3.14	1670		c	0.0025
CaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	2.31	d.		c	0.02(25.4°)
CaH <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	2.22	d.		c	1.8(30°)
Ca <sub>3</sub> P <sub>2</sub> O <sub>7</sub>	3.09	1230		c	sl. sol.
Ca(H <sub>2</sub> PO <sub>3</sub> ) <sub>2</sub>		d.		c	sol.
3Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·CaFCl	3.14	1270		c	v. sl. sol.
CaSO <sub>4</sub>	2.96	1297		c	cf. 2 aq.
CaSO <sub>4</sub> ·2H <sub>2</sub> O	2.32	2 aq. 163		c	0.208(25°)
CaS	2.81			c	hydr.
CaSO <sub>3</sub>				c	0.17(15°)
CaSeO <sub>4</sub> ·2H <sub>2</sub> O	2.76			c	2 aq. 7.6(20°)
<i>Carbon</i>					
C (diamond)	3.51			c	
C (graphite)	2.25		4827	bl	v. sl. sol.
CO	1.081	— 205	— 191.5	c	0.0044(0°), 0.0018(50°)
CO <sub>2</sub>	s. 1.53	s. — 55.6	— 78.5	c	0.335(0°), 0.145(20°), 0.06(60°)
C <sub>3</sub> O <sub>2</sub>	1.110	— 107	6.3	c	giv. malonic acid
CBr <sub>4</sub>	1.342	{ α48.4 β90.1 }	189.5	w	v. sl. sol.
CCl <sub>4</sub>	1.159	— 24.0	77.1	c	0.08(20°)
CF <sub>4</sub>			— 127.9	c	sl. sol.
Cl <sub>4</sub>	4.32	d.		r	hydr.
COS	1.124	— 138	— 43.2	c	0.122(25°)
CS <sub>2</sub>	1.126	— 110.8	46.3	c	0.18(20°)
C <sub>2</sub> N <sub>2</sub>	0.87	— 27.1	— 20.5	c	sl. sol.: (C <sub>2</sub> N <sub>2</sub> ) <sub>n</sub> more sol.
<i>Cerium</i>					
Ce	6.9	765	1400	gy	v. sl. sol.
Ce <sub>2</sub> O <sub>3</sub>	6.9			c	v. sl. sol.
CeO <sub>2</sub>	7.3	1950		l-y	v. sl. sol.
CeCl <sub>3</sub>	3.92	848		c	sol.
Ce <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O				c	v. sl. sol.
CeF <sub>3</sub>	5.8	1324		c	v. sl. sol.
Ce(IO <sub>3</sub> ) <sub>4</sub>				c	0.015(20°)
Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O		3 aq. 150	d. 200	r	sol.
Ce(NO <sub>3</sub> ) <sub>4</sub>				y	sol.
Ce <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O		8 aq. 110		c	4 × 10 <sup>-5</sup> (25°)
Ce <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	3.91			c	8 aq. 8.7(20°)
Ce(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O				y	sol.
<i>Cesium</i>					
Cs	1.90	28.4	690	sil	CsOH + H <sub>2</sub>
Cs <sub>2</sub> O	4.36			or	giv. CsOH
Cs <sub>2</sub> O <sub>2</sub>	4.25	400		gy	d.
CsO <sub>2</sub>	3.77	600		y	giv. CoOH + HO <sub>2</sub> <sup>-</sup>
CsOH	3.67	272.5		c	79.4(15°)
CsBr	4.44	636	1300	c	55(25°)
Cs <sub>2</sub> CO <sub>3</sub>			d. 610	c	v. sol.
CsCl	3.97	642	1300	e	65(20°), 73(100°)
CsF	3.59	715	1251	c	1.5 aq. v. sol.
CsI	4.51	621	1280	c	28(0°), 51.5(35.6°)
CsNO <sub>3</sub>	3.68	407	d.	c	18.7(20°), 66.3(100°)

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
$\text{Cs}_2\text{SO}_4$	4.24	1010		c	61(20°)
<i>Chlorine</i>					
$\text{Cl}_2$	s. 1.9	- 101.6	- 34.7	l-y	0.63(25°)
$\text{Cl}_2 \cdot 8\text{H}_2\text{O}$	1.23	d. 9.6		l-y	1.85(20°) Under P.
$\text{HClO}_4 \cdot 7\text{H}_2\text{O}$	1.28	d.		c	v. sol.
$\text{HClO}_4$	1.177	- 112		c	1 aq. 77.7(17°)
$\text{Cl}_2\text{O}$	0.00385	- 20	2.0	y-r	2 vol/vol $\text{H}_2\text{O}$ at 0°
$\text{ClO}_2$	0.00298	- 76	11	r	10.8(18°)
<i>Chromium</i>					
Cr	7.1	1545	2482	sil	not sol.
$\text{CrO}_3$	2.7	d. 190	d.	r	62.8(25°)
$\text{Cr}_2\text{O}_3$	5.21	1900		gr	v. sl. sol.
$\text{Cr}(\text{OH})_3$				y-br	evol. 2 H
$\text{Cr}(\text{OH})_3 \cdot 2\text{H}_2\text{O}$				gr	v. sl. sol.
$\text{CrCl}_3$	2.75			bl	v. sol.
$\text{CrCl}_3$	2.7			v	70(25°) v. slowly sol.
$\text{Cr}_2\text{C}_3$	6.68	1890	3810	gr	not sol.
$\text{CrF}_3$	3.8	> 1000		gr	v. sol.
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$		36.5		pu	sol.
$\text{Cr}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$				bl.gr	sl. sol.
$\text{CrSO}_4 \cdot 7\text{H}_2\text{O}$				bl	12 g. 7 aq/100 g. $\text{H}_2\text{O}$ (0°)
$\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	1.7	12 aq. 100		v	120 g. 18 aq/100 g. $\text{H}_2\text{O}$ -(20°)
$\text{Cr}_2\text{S}_3$	3.7			d-br	hydr. slowly
<i>Cobalt</i>					
Co	8.9	1490	2900	gy-w	not sol.
CoO	5.68	d. 1800		br	v. sl. sol.
$\text{Co}_2\text{O}_3$	5.18	d. 900		br	v. sl. sol.
$\text{Co}_3\text{O}_4$	6.07			bl	v. sl. sol.
$\text{Co}(\text{OH})_2$	3.60	d.		r	v. sl. sol.
$\text{Co}(\text{OH})_3$				bl	$3.2 \times 10^{-4}$
$\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$	1.72			v	sol.
$\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$	2.9			r	v. sl. sol.
$\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$		d. 100		r	67(60°)
$\text{CoCO}_3$	4.13	d.		r	v. sl. sol.
$\text{Co}_2(\text{CO})_8$	1.73	51	d. 135	or	v. sl. sol.
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	1.92	an. 727	an. 1050	r	33.3(20°)
$\text{CoCl}_2$	2.94	d.		r	sol.
$\text{CoI}_2$	5.68			v	2 aq. 79(46°)
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.88	< 100		r	49.7(18°)
$\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$				l-r	v. sl. sol.
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	1.95	an. 989		r	26.6(20°), 45.3(100°)
$\text{Co}_2(\text{SO}_4)_3$				bl	hydr.
CoS	5.45	< 1100		br	0.00038
<i>Columbium</i>					
Cb	8.4	1950	3300	gr	not sol.
$\text{Cb}_2\text{O}_5$	4.61	1520		c	v. sl. sol.
$\text{CbF}_5$	3.29	75.5	225	c	hydr.
$\text{CbCl}_5$	2.75	194	240.5	y	hydr.
$\text{CbOCl}_3$			s. 400	c	sol., hydr.
<i>Copper</i>					
Cu	8.92	1084	2595	r	v. sl. sol.
$\text{Cu}_2\text{O}$	6.0	1230	1800	r	v. sl. sol.
CuO	6.4	d. 1026 at 153 mm. $\text{O}_2$			
$\text{Cu}(\text{OH})_2$	3.68	d.		bk	v. sl. sol.
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$	1.88	115	d. 240	bl	v. sl. sol.
$\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$		d. 150		gr	18.5(21.5°)
$\text{Cu}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$				bl	sol. giv. $\text{Cu}(\text{NH}_3)_4^{++}$
$\text{CuHAsO}_2$		d.		bl-gr	v. sl. sol.
CuBr	4.72	504	1355	gr	v. sol.
				br	sl. sol.

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
CuBr <sub>2</sub>		498		bl	sol.
Cu <sub>2</sub> CO <sub>3</sub>	4.40	d.		y	v. sl. sol.
2CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub>	3.88	d. 220		bl	v. sl. sol.
CuCl	3.53	430	1490	c	1.5(25°)
CuCl <sub>2</sub> ·2H <sub>2</sub> O	2.39	d. 110	d.	gr	43.5(20°)
CuCl <sub>2</sub>	3.054	498	d.	l-y	
CuCN		474		c	v. sl. sol.
Cu <sub>2</sub> Fe(CN) <sub>6</sub> ·7H <sub>2</sub> O				r-br	v. sl. sol.
CuI	5.62	605	1336	gy-br	0.0004(18°)
Cu(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	2.05	d. 26.4	d.	bl	55.6(20°)
Cu <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O				bl	sl. sol.
CuSO <sub>4</sub>	3.6	d. 620		c	
CuSO <sub>4</sub> ·5H <sub>2</sub> O	2.29		1 aq. d. 230	bl	18.7(25°), 42.4(100°)
Cu <sub>2</sub> S, Rhom.	5.6	1100		bk	
Cu <sub>2</sub> S, Cub.	5.76	1130		bk	0.00005(18°)
CuS	4.6	d. 220		bk	0.000033(18°)
CuCNS	2.85	1084		c.	v. sl. sol.
<i>Fluorine</i>					
F <sub>2</sub>	1.114	- 223	- 188.2	c	d. O <sub>3</sub> + HF
F <sub>2</sub> O	1.165	- 223.8	- 144.8	c	v. sl. sol.
<i>Gadolinium</i>					
Gd					evol. H <sub>2</sub>
Gd <sub>2</sub> O <sub>3</sub>	7.41			c	v. sl. sol.
GdCl <sub>3</sub>	4.62	628		c	sol.
Gd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	4.14			c	8 aq. 2.4(25°)
Gd <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·10H <sub>2</sub> O		d. 110		c	0.11(25°)
<i>Gallium</i>					
Ga	5.91	29.5	2071	sil	not sol.
GaCl <sub>3</sub>		175	535	c	v. sol.
GaCl <sub>3</sub>	1.237	75.5	217	c	v. sol.
<i>Germanium</i>					
Ge	5.36	958.5	2700	sil	
GeO <sub>2</sub>	4.70	1000			0.40(20°)
GeH <sub>4</sub>	1.152	- 165	- 89.1	c	sl. sol.
Ge <sub>2</sub> H <sub>6</sub>	1.198	- 109	29	c	sl. sol.
GeCl <sub>4</sub>	1.187	- 49.5	84	c	hydr.
GeBr <sub>4</sub>	1.313	26.1	189	gy	hydr.
GeI <sub>4</sub>	4.32	144	375	y	hydr.
<i>Gold</i>					
Au	19.3	1063	2966	y-w	not sol.
Au <sub>2</sub> O <sub>3</sub>		d. 160		bl	v. sl. sol.
AuOH		d.		r-br	giv. Au <sub>2</sub> O <sub>3</sub> + Au
Au(OH) <sub>3</sub>		d. 250		y-br	v. sl. sol.
AuBr		d. 115		y-gy	v. sl. sol.
AuBr <sub>3</sub>		d. 160		br	sol.
HAuBr <sub>4</sub> ·5H <sub>2</sub> O		27		r	sol.
AuCl	7.4	d. 289.5		y	v. sl. sol.
AuCl <sub>3</sub>	3.9	d. 254	s. 265	y-r	40
Au <sub>2</sub> Cl <sub>4</sub>	5.1	d. 250		r	d.
AuCN		d.		y	v. sl. sol.
Au(CN) <sub>3</sub> ·6H <sub>2</sub> O		d. 50			v. sol.
Au <sub>2</sub> S <sub>2</sub>		d. 140		bk	v. sl. sol.
Au <sub>2</sub> S <sub>3</sub>	8.75	d. 197		br	v. sl. sol.
Au <sub>2</sub> O <sub>3</sub> ·2SO <sub>3</sub> ·H <sub>2</sub> O					sol.
HAu(NO <sub>3</sub> ) <sub>4</sub> ·3H <sub>2</sub> O	2.84	d. 72		r-y	sol.
<i>Hafnium</i>					
Hf	12.1	1700	> 3200	r-gy	not sol.
HfO <sub>2</sub>	9.68	2812		c	v. sl. sol.
HfOCl <sub>2</sub> ·8H <sub>2</sub> O				c	sol.
K <sub>2</sub> HfF <sub>6</sub>				c	3.0(20°)

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
<i>Helium</i>					
He		- 272 (Pressure)	- 268.9	c	0.00858 vol/vol H <sub>2</sub> O(20°)
<i>Hydrogen</i>					
H <sub>2</sub>	1. 0.08	- 259.15	- 252.7	c	1.93 × 10 <sup>-4</sup> (0°) 1.56 × 10 <sup>-4</sup> (25°)
HBr	1. 2.16	- 87.0	- 66.7	c	65.9(25°)
HCl	1. 1.194	- 114.2	- 85	c	64.2(20°), 61.6(50°)
HCN	0.699	- 13.1	26	c	v. sol.
HF	1. 0.988	- 83.0	19.5	c	52.6-(35°)
HI	1. 2.84	- 50.8	- 36.7	c	20.3-(10°)
HN <sub>3</sub>		- 80	37	c	sol.
H <sub>2</sub> S	1. 0.96	- 85.5	- 60.3	c	0.38(20°)
H <sub>2</sub> Se	1. 2.12	- 64	- 41.3	c	2.7 vol/vol H <sub>2</sub> O(22.5°)
H <sub>2</sub> Te	1. 2.57	- 49	- 2.2	c	sol.
H <sub>2</sub> O <sub>2</sub>	1. 1.44	- 1.7	158	c	v. sol.
H <sub>2</sub> O	1.0(4°)	0	100	c	
<i>Iodine</i>					
I <sub>2</sub>	4.93	113.0	183	pu-bk	0.0181(11°), 0.092(55°)
HIO <sub>3</sub>	4.63	d. 110		c	cf. I <sub>2</sub> O <sub>5</sub>
H <sub>5</sub> I O <sub>6</sub>				c	v. sol.
IO <sub>2</sub>	4.21	d. 130		y	giv. HIO <sub>3</sub> + I <sub>2</sub>
I <sub>2</sub> O <sub>5</sub>	4.80	d. 300		c	2 aq. 71.7(16°)
ICl <sub>α</sub>	1. 3.24	27.2	97	r-br	hydr. HIO + Cl <sup>-</sup>
ICl <sub>β</sub>	1. 3.24	13.9		r-br	hydr.
ICl <sub>3</sub>	3.11	33	s. 101 (16 atm.)	y	hydr.
IBr	4.41	42	116	pu-bk	hydr.
IF <sub>5</sub>	1. 3.5	- 8	97	c	hydr.
<i>Indium</i>					
In	7.3	156.4	1450	sil	not sol.
In <sub>2</sub> O <sub>3</sub>	7.18			l-y	v. sl. sol.
InCl <sub>3</sub>	4.0			c	v. sol.
InI <sub>3</sub>		199		y	sol.
In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	3.44			c	sol.
<i>Iridium</i>					
Ir	22.4	2350	4800	sil	not sol.
IrO <sub>2</sub>				gy	v. sl. sol.
IrCl <sub>2</sub>		d. 775		br	v. sol.
IrCl	5.30	d. 763		d-gr	sol. if hydrated
IrCl <sub>4</sub> ·2NH <sub>4</sub> Cl	2.86	d.		d-r	0.9(27°)
IrCl <sub>3</sub> ·3NH <sub>4</sub> Cl				gr-br	sol.
Ir <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·24H <sub>2</sub> O		106		y-r	sol.
<i>Iron</i>					
Fe	7.86	1530	2735	gy	not sol.
FeO		1380		c	v. sl. sol.
Fe <sub>2</sub> O <sub>3</sub>	5.12	d. 1560		r	v. sl. sol.
Fe <sub>3</sub> O <sub>4</sub>	5.2	d. 1538		bk	v. sl. sol.
Fe(OH) <sub>2</sub>				gr	0.0096(18°)
Fe(OH) <sub>3</sub>	3.4-3.9	1 aq. 500		r-br	v. sl. sol.
FeOH(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>				r	v. sl. sol.
FeSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	1.86			bl-gr	25.0(25°)
FeAs	7.83	1020		w	v. sl. sol.
FeBr <sub>3</sub> ·6H <sub>2</sub> O		27		r	v. sol.
FeBr <sub>2</sub>	4.64			r	6 aq. 54.3(25°)
FeCO <sub>3</sub>	3.8	d.		gr-br	0.0065(20°)
Fe <sub>3</sub> C	7.4	1837		gy	not sol.
Fe(CO) <sub>5</sub>	1.46	- 21	102.5	gr	v. sl. sol.
FeCl <sub>2</sub> ·4H <sub>2</sub> O	1.93		an. 1026	gr-w	41.5(25°)

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
FeCl <sub>3</sub> ·6H <sub>2</sub> O		37	280	r-y	47.9(20°)
FeCl <sub>3</sub>	2.8	319	319	r	
Fe <sub>4</sub> [Fe(CN) <sub>6</sub> ] <sub>3</sub>		d.		bl	v. sl. sol.
FeI <sub>2</sub> ·4H <sub>2</sub> O	2.87	(an.) 177		gr	v. sol.
Fe(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O		d. 60		gr-w	45.5(20°)
Fe(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	1.68	47.2	d.	gy	v. sol.
Fe <sub>2</sub> N	6.35	d.		gy	not sol.
FeC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O	2.28	d. 160		y	0.022
Fe <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>		d. 100		y	v. sol.
Fe <sub>3</sub> P	6.74	1100		gy	not sol.
Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	2.58			bl	v. sl. sol.
FePO <sub>4</sub> ·2H <sub>2</sub> O	2.87			y	v. sl. sol.
FeSO <sub>4</sub> ·7H <sub>2</sub> O	1.89	64	d.	bl-gr	21(20°)
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	2.1			y	v. sol.
FeS	4.8	1195		bl	0.0006(18°)
FeS <sub>2</sub>	5.0			y	v. sl. sol.
Fe <sub>2</sub> S <sub>3</sub>	4.3	d.		y-gr	v. sl. sol. giv. FeS + S
Fe(CNS) <sub>3</sub> ·3H <sub>2</sub> O				r	v. sol.
<i>Krypton</i>					
Kr		- 156.6	- 152.9	c	sl. sol.
<i>Lanthanum</i>					
La	6.15	826	1800	gy	La(OH) <sub>3</sub> + H <sub>2</sub>
La <sub>2</sub> O <sub>3</sub>	6.51	> 2000	4210	c	giv. sl. OH <sup>-</sup>
La <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> ·8H <sub>2</sub> O	2.7			c	v. sl. sol.
LaCl <sub>3</sub>	3.95	907		c	sol.
La(IO <sub>3</sub> ) <sub>3</sub>				c	1.7(25°)
La(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O		40	d. 126	c	60.2(25°)
La <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	2.82	d.		c	2.91(0°), 1.86(30°)
<i>Lead</i>					
Pb	11.34	327.4	1744	gy	
PbO	9.53	890		y	0.002(20°)
PbO <sub>2</sub>	9.38	d. 290		br	v. sl. sol.
Pb <sub>3</sub> O <sub>4</sub>	9.1	d. 500		r	v. sl. sol.
Pb(OH) <sub>2</sub>		d. 145		c	0.016(20°)
Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	2.55	d. 75		c	v. sol. hydr.
Pb <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>	7.30	1042		c	v. sl. sol.
Pb(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	1.166		83 (14 mm.)	c	v. sl. sol.
Pb(BO <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O	5.60	high temp.		c	v. sl. sol.
PbBr <sub>2</sub>	6.66	488	914	y	0.455(0°), 4.55(100°)
PbCO <sub>3</sub>	6.6	d. 315		c	0.00015(20°)
2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>	6.14	d. 400		l-y	v. sl. sol.
PbCl <sub>2</sub>	5.85	498	954	c	0.637(0°), 3.20(100°)
PbCl <sub>4</sub>	1.318	- 15	d.	c	hydr. evol. Cl <sub>2</sub>
PbCrO <sub>4</sub>	6.3	844		y	7 × 10 <sup>-6</sup> (20°)
PbF <sub>2</sub>	8.24	824	1290	c	0.068(27°)
PbI <sub>2</sub>	6.16	412	822	y	0.044(0°), 0.434(100°)
Pb(IO <sub>3</sub> ) <sub>2</sub>		d. 300		c	0.003(25°)
Pb(NO <sub>3</sub> ) <sub>2</sub>	4.53	d. 470		c	34.3(20°)
PbC <sub>2</sub> O <sub>4</sub>	5.28	d. 300		c	0.00015(18°)
PbCl <sub>2</sub> ·PbO	7.21	d. 524		c	v. sl. sol.
Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	ca 7.1	1014		c	0.000014(20°)
Pb(PO <sub>3</sub> ) <sub>2</sub>		800		c	v. sl. sol.
PbS	7.5	1114	1281	bk	2.9 × 10 <sup>-6</sup> (18°)
PbSO <sub>3</sub>				c	v. sl. sol.
PbSO <sub>4</sub>	6.2	1087		c	0.0042(20°)
Pb <sub>2</sub> O(SO <sub>4</sub> )	6.92	977		c	v. sl. sol.
Pb(CNS) <sub>2</sub>	3.82	d. 190		y	0.5(20°)
PbSiO <sub>3</sub>	6.49	766		c	v. sl. sol.
<i>Lithium</i>					
Li	0.53	179	1372	sil	giv. LiOH + H <sub>2</sub>



FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
Li <sub>2</sub> O	2.01	> 1700		c	giv. LiOH
LiOH	2.54	462		c	11.3(10°), 14.9(100°)
LiC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ·2H <sub>2</sub> O		70	d.	c	75(15°)
LiHCO <sub>3</sub>				c	5.5(13°)
LiBr	3.46	552	1310	c	2 aq. 66.2(34°)
Li <sub>2</sub> CO <sub>3</sub>	2.11	618		c	1.51(0°), 0.725(100°)
LiCl	2.07	614	1353	c	1 aq. 45.9(25°)
LiClO <sub>4</sub>	2.43	236	d. 410	c	37.4(25°)
LiF	2.30	870	1670	c	0.26(18°)
LiH	0.82	680		c	giv. LiOH + H <sub>2</sub>
LiI		440	1171	c	3 aq. 62(20°)
LiNH <sub>2</sub>	1.18	390		c	hydr.
LiNO <sub>2</sub>	2.4	250		c	3 aq. 42.9(22°)
Li <sub>3</sub> PO <sub>4</sub>	2.54	837		c	0.04
Li <sub>2</sub> S	1.66	847		c	v. sol.
Li <sub>2</sub> SO <sub>4</sub>	2.22	857		c	1 aq. 25.7(20°)
Li <sub>2</sub> SiO <sub>3</sub>	2.33	1177		c	sol.
<i>Magnesium</i>					
Mg	1.74	650	1107	w	giv. Mg(OH) <sub>2</sub> slowly
MgO	3.65	2642		c	giv. Mn(OH) <sub>2</sub> slowly
Mg(OH) <sub>2</sub>	2.36	d.		c	0.0009(18°)
Mg(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	1.45			c	v. sol.
MgNH <sub>4</sub> AsO <sub>4</sub> ·6H <sub>2</sub> O	1.93	d.		c	0.021(20°)
MgNH <sub>4</sub> PO <sub>4</sub> ·6H <sub>2</sub> O	1.72	d.		c	0.02
MgBr <sub>2</sub>	3.72	711		c	6 aq. 49.1(20°)
MgCO <sub>3</sub>	3.08	d. 350		c	0.01(18°) hydr.
3MgCO <sub>3</sub> ·Mg(OH) <sub>2</sub> ·3H <sub>2</sub> O	2.18			c	v. sl. sol.
MgCl <sub>2</sub> ·6H <sub>2</sub> O	1.56	an. 712	an. 1418	c	35.3(20°)
MgF <sub>2</sub>	3.0	1396		c	0.009(20°)
MgI <sub>2</sub>	4.25			c	8 aq. 59.7(18°)
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	1.46	95	5 aq. 330	c	43.1(18°)
MgC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O		d.		c	0.07
MgHPO <sub>4</sub> ·3H <sub>2</sub> O	2.10			c	0.3
Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	2.60	1383		c	v. sl. sol.
MgSO <sub>4</sub>	2.66	1185		c	
MgSO <sub>4</sub> ·7H <sub>2</sub> O	1.68	d. 70		c	26.8(25°)
MgS	2.8	d.		gy	hydr.
<i>Manganese</i>					
Mn	7.2	1220	2151	gy-pk	giv. Mn(OH) <sub>2</sub> + H <sub>2</sub>
Mn <sub>2</sub> O <sub>7</sub>	l. 2.4	< - 20	exp.	r	v. sol.
MnO	5.18	1650		gy-gr	v. sl. sol.
Mn <sub>2</sub> O <sub>3</sub>	4.8	d. 1080		bk	v. sol. sl.
MnO <sub>2</sub>	5.02			bk	v. sl. sol.
Mn <sub>2</sub> O <sub>4</sub>	4.7	v. high		bk	v. sl. sol.
Mn(OH) <sub>2</sub>	3.26	d.		l-pk	0.002
Mn <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	3.26	d.		br	v. sl. sol.
Mn(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	1.59			l-r	3
NH <sub>4</sub> MnPO <sub>4</sub> ·7H <sub>2</sub> O				c	0.003
MnBr <sub>2</sub>	4.38			ro-r	4 aq. 58.8(20°)
MnCO <sub>3</sub>	3.12	d.		ro	0.0065(25°)
MnCl <sub>2</sub>	2.98	650	1190	pk	
MnCl <sub>2</sub> ·4H <sub>2</sub> O	2.01	d. 58.01		r-or	43.6(25°)
MnF <sub>2</sub>	3.98	856		ro	0.18(25°)
MnF <sub>3</sub>	3.54			r	hydr.
MnI <sub>2</sub>	5.01			ro	v. sol.
Mn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	1.82	d. 25.8		ro	63(25°)
MnC <sub>2</sub> O <sub>4</sub> ·2½H <sub>2</sub> O	2.43	d. 150		pk-ro	0.03(25°)
Mn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·7H <sub>2</sub> O				ro	sl. sol.
Mn <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	3.71			ro	sl. sol.
MnSiO <sub>3</sub>	3.48	1273		r	v. sl. sol.

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
MnS	3.99	d. 1620		l-ro	0.0007
MnS <sub>2</sub>	3.46			r	d.
MnSO <sub>4</sub>	3.25	700		r	
MnSO <sub>4</sub> ·5H <sub>2</sub> O	2.11	d.		ro	39.3(25°)
<i>Mercury</i>					
Hg	14.19	— 38.87	356.9	sil.	not sol.
Hg <sub>2</sub> O	9.8	d. 100		bk	v. sl. sol.
HgO	11.14	d. 100	d.	y and	
				r	0.00515(25°)
Hg(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	3.27	d.		c	25 g./100 g. H <sub>2</sub> O(25°)
Hg <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>				y	sl. sol.
Hg <sub>2</sub> Br <sub>2</sub>	7.31		s. 345	y	3.9 × 10 <sup>-6</sup> (25°)
HgBr <sub>2</sub>	6.05	241	319	l-y	0.6(25°)
Hg <sub>2</sub> CO <sub>3</sub>		d. 130		y	v. sl. sol.
Hg <sub>2</sub> Cl <sub>2</sub>	7.15	302	383.7	c	0.0003(25°)
HgCl <sub>2</sub>	5.44	277	304	c	6.89(25°), 35.1(100°)
Hg <sub>2</sub> CrO <sub>4</sub>		d.		r	sl. sol.
Hg(CN) <sub>2</sub>	4.00	d.		c	8.5(20°)
Hg <sub>2</sub> F <sub>2</sub>	8.73	570		c	sol.
HgF <sub>2</sub>	8.95	d. 645	650	c	sol.
Hg <sub>2</sub> I <sub>2</sub>	7.70	d. 290	d.	y	2 × 10 <sup>-8</sup> (25°)
HgI <sub>2</sub>	6.27	250	354	y	0.004(17.5°)
Hg <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	4.78	70		c	sol.
Hg(NO <sub>3</sub> ) <sub>2</sub> · $\frac{1}{2}$ H <sub>2</sub> O	4.3	79		c	sol.
NH <sub>4</sub> g <sub>2</sub> Br·3NH <sub>4</sub> Br		d. 180		c	v. sl. sol.
Hg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>				c	v. sl. sol.
Hg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>				w to y	v. sl. sol.
Hg <sub>2</sub> S				bk	v. sl. sol.
HgS	α8.1 β7.7	s. 580 s. 446		r bk	v. sl. sol.
Hg <sub>2</sub> (SO <sub>4</sub> )	7.56	d.	d.	c	0.06(25°)
HgSO <sub>4</sub>	6.47	850		c	sol.
<i>Molybdenum</i>					
Mo	10.2	2620	4804	gy	not sol.
MoO <sub>3</sub> ·2H <sub>2</sub> O	3.12			y	0.18(23°), 1.70(70°)
MoO <sub>2</sub>	4.52			r	v. sl. sol.
Mo <sub>2</sub> O <sub>3</sub>				y to bl	v. sl. sol.
MoO <sub>3</sub>	4.50	785	1151	y	0.107(18°), 1.705(70°)
MoCl <sub>2</sub>		d.		y	v. sl. sol.
MoCl <sub>3</sub>		d.		w	sol.
MoCl <sub>5</sub>		194	268	bl	v. sol.
MoF <sub>6</sub>		17	36	c	hydr.
MoOF <sub>4</sub>	3.0	98	180	c	sol.
MoS <sub>2</sub>	4.8	1185		bl	v. sl. sol.
Mo <sub>2</sub> S <sub>3</sub>	5.91			gy	v. sl. sol.
MoS <sub>3</sub>		d.		r-br	sl. sol.
<i>Neon</i>					
Ne		— 248.5	— 245.9	c	1.5 cc./100 cc. H <sub>2</sub> O(20°)
<i>Nickel</i>					
Ni	8.9	1452	2732	sil	not sol.
NiO	7.45			gr	v. sl. sol.
Ni <sub>3</sub> O <sub>4</sub> ·2H <sub>2</sub> O	3.41			gy	v. sl. sol.
NiO <sub>2</sub> ·xH <sub>2</sub> O		d.		bk	v. sl. sol.
Ni(OH) <sub>2</sub>	4.36			gr	0.0013
Ni(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	1.80	d.		gr	sol.
NiCl <sub>2</sub> ·NH <sub>4</sub> Cl·6H <sub>2</sub> O	1.64			gr	v. sol.
NiSO <sub>4</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	1.92			gr	25(3.5°)
Ni <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub>	4.98			y	v. sl. sol.
NiBr <sub>2</sub>	4.64			y	6 aq. 57.3(25°)
NiCO <sub>3</sub>		d.		l-gr	0.0093(25°)

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
$2\text{NiCO}_3 \cdot 3\text{Ni(OH)}_2$ $\cdot 4\text{A}_2\text{O}$		d.		l-gr	v. sl. sol.
$\text{Ni(CO)}_4$	1.1.31	-25	43	c	0.018(9.8°)
$\text{NiCl}_2$	3.54		987	y	53.8(0°), 87.6(100°)
$\text{Ni(ClO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.07	d. 80		d-r	v. sol.
$\text{Ni(ClO}_3)_2 \cdot 6\text{NH}_3$	1.52	180			giv. $\text{Ni(NH}_3)_4^{++}$
$\text{Ni(CN)}_2 \cdot 4\text{H}_2\text{O}$		4 aq. 200		gr	sol.
$\text{NiI}_2$		s.		bl	6 aq. 59.7(20°)
$\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.05	d. 56.7		gr	v. sol.
$\text{Ni}_2\text{P}$	6.31	1112		gy	not sol. $\text{HNO}_3$
$\text{Ni(H}_2\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.82	d.		gr	sol.
$\text{Ni}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$				gr	v. sl. sol.
$\text{NiS}$	4.6	797		bk	0.00036(18°)
$\text{NiSO}_4$	3.68	d. 840		y	
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	1.948	99		gr	25.5(15°)
<i>Nitrogen</i>					
$\text{N}_2$	1. 0.83	-209.96	-195.8	c	0.0019(20°)
$\text{HNO}_3$	1. 1.502	-47.1	86	c	v. sol.
$\text{NO}$	1. 1.27	-163.6	151.7	c	0.0056(25°)
$\text{NO}_2(\text{N}_2\text{O}_4)$	1. 1.45	-9.3	21.3	y-br	giv. $\text{HNO}_2 + \text{HNO}_3$
$\text{N}_2\text{O}$	1. 1.23	-102.4	-88.5	c	0.121(20°)
$\text{N}_2\text{O}_3$	1. 1.45	-102	3.5	bl	giv. $\text{HNO}_2$
$\text{N}_2\text{O}_5$		30	32.5	c	giv. $\text{HNO}_3$
$\text{NH}_2 \cdot \text{NH}_2$	1. 1.01	1.4	113.5	c	v. sol.
$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$	1. 1.03	< -40	118.5	c	v. sol.
$\text{N}_2\text{H}_4 \cdot 2\text{HNO}_3$		104		c	v. sol.
$\text{N}_2\text{H}_4 \cdot \text{HCl}$		89		c	sol.
$\text{N}_2\text{H}_4 \cdot 2\text{HCl}$	1.42	198		c	sol.
$\text{N}_2\text{H}_4 \cdot \text{HClO}_3$		exp. 80		c	sol.
$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$	1.37	254		c	3.0(22°)
$\text{NH}_2\text{OH}$	1.35	34	56.5	c	sol. $\text{H}_2\text{O}$ , alcohol
$\text{NH}_2\text{OH} \cdot \text{HCl}$	1.67	151		c	sol.
$(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$		170		c	sol.
$\text{N}_2\text{H}$		-80	37	c	sol.
$\text{NH}_2\text{NO}_2$		d. 72		c	hydr.
$\text{NOF}$		-134	-56	c	gw. $\text{HNO}_2 + \text{HF}$
$\text{NCl}_3$	1. 1.65		< 71	y	hydr.
$\text{NOCl}$	1. 1.41	-64.5	-6.4	y-r	sl. sol.
$\text{NOBr}$		-55.5	-2	d-br	hydr.
$\text{NOBr}_3$	1. 2.64	-40	ca. 32	br	hydr.
$\text{NH}_3\text{I}_2$	1. 2.46	-2	d. 15	d-br	v. sl. sol.
$\text{NI}_3 \cdot \text{NH}_3$	3.5	d. > 20		d-br	v. sl. sol.
$\text{N}_2\text{S}_5$	1. 1.90	11		r	d.
$\text{N}_4\text{S}_4$	2.22	178	s. 135	y-r	giv. $\text{NH}_3$ , $\text{SO}_2$ , $\text{H}_2\text{S}_2\text{O}_5$
$\text{N}_2\text{O}_7 \cdot 2\text{SO}_3$	2.14	230	357.3	c	hydr.
$\text{NO}_2\text{SO}_3\text{H}$		d. 73		c	hydr.
$\text{SO}_2(\text{NH}_2)_2$		92		c	hydr.
$\text{NH}_2\text{SO}_3\text{H}$	2.03	d. 205		c	hydr.
$\text{NH}(\text{SO}_3\text{NH}_4)_2$	1.96	357		c	giv. $(\text{NH}_4)_2\text{SO}_4$
<i>Osmium</i>					
$\text{Os}$	22.48	2700	> 5300	bl	not sol.
$\text{OsO}_2$	7.9			bl-r	v. sl. sol.
$\text{OsO}_4\text{w}$	4.91	42.0	130	y	5.8(15°)
$\text{OsO}_4\text{y}$		39.5	130	c	
$\text{OsCl}_2$				gr	sl. sol.
$\text{OsCl}_3$				br	sl. sol.
$\text{OsCl}_4$				r to y	sl. sol.
$\text{OsF}_6$			203		hydr.
$\text{OsF}_8$		34.5	47.3	c	giv. $\text{OsO}_4$
$\text{OsS}_2$				y	sl. sol.
$\text{OsS}_4$		d.		bl	not sol.

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
<i>Oxygen</i>					
O <sub>2</sub>	1. 1.13	— 218.7	— 183.0	l-bl	0.00434(20°), 0.00079 (90°)
O <sub>3</sub>		— 251.4	— 111.1	bl	0.0026(15°)
<i>Palladium</i>					
Pd	12.0	1555	2200	sil	not sol.
PdO		d. 877		bk	v. sl. sol.
PdO <sub>2</sub>		d. 200		bk	v. sl. sol.
Pd(OH) <sub>2</sub>				br	v. sl. vol.
PdBr <sub>2</sub>				br	v. sl. sol.
PdCl <sub>2</sub>		d. 500		d-br	sl. sol.
PdI <sub>2</sub>		d. 350		bk	v. sl. sol.
Pd(NO <sub>3</sub> ) <sub>2</sub>		d.		y	sol.
PdS		950		bk	v. sl. sol.
Pd <sub>2</sub> S	7.3	d. 800		gr	
PdS <sub>2</sub>		d.		br	v. sl. sol.
PdSO <sub>4</sub> ·2H <sub>2</sub> O				br	v. sol.
(NH <sub>4</sub> ) <sub>2</sub> PdCl <sub>4</sub>	2.17			y-gr	sol.
(NH <sub>4</sub> ) <sub>2</sub> PdCl <sub>6</sub>	2.42			r	sl. sol.
Pd(CO) <sub>2</sub> Cl <sub>2</sub>		1.42		y-r	d.
<i>Phosphorus</i>					
P <sub>4</sub> yellow	1.82	44.2	280	y	0.0003(15°)
P <sub>4</sub> red	2.35	590 (43 atm.)	s. 417	r	v. sl. sol.
P <sub>2</sub> O <sub>3</sub>	2.13	23.8	173	c	giv. H <sub>3</sub> PO <sub>3</sub>
P <sub>2</sub> O <sub>4</sub>	2.53	> 100	s. ca. 180	c	giv. H <sub>3</sub> PO <sub>3</sub>
P <sub>2</sub> O <sub>5</sub> α	2.39	569	591	c	giv. H <sub>3</sub> PO <sub>4</sub>
H <sub>3</sub> PO <sub>3</sub>	1.65	73.6	d. 200	y	v. sol.
H <sub>3</sub> PO <sub>2</sub>	1.49	17.4	d.	c	v. sol.
H <sub>3</sub> PO <sub>4</sub>	1.83	42.35	d.	c	86(24°)
HPO <sub>3</sub>	2.2-2.5	sub. at w. heat		c	sol.
H <sub>4</sub> P <sub>2</sub> O <sub>7</sub>		55		c	89(23°)
PBr <sub>3</sub>	1. 2.85	— 40	172.9		hydr.
PBr <sub>5</sub>			106	y	hydr.
PCl <sub>3</sub>	1. 1.57	— 111.8	74.2	c	hydr.
PCl <sub>5</sub>		148	162	l-y	hydr.
P <sub>2</sub> Cl <sub>4</sub>		— 28	180	c	hydr.
POCl <sub>3</sub>	1. 1.67	1.1	105.1	c	hydr.
PH <sub>4</sub> Cl		28 (46 atm.)		c	sol.
PF <sub>3</sub>	3.02	— 160	— 95	c	hydr.
PF <sub>5</sub>	4.49	— 83	— 75	c	hydr.
POF <sub>3</sub>	3.63	— 68	— 40	c	hydr.
PH <sub>3</sub>	1. 0.75	— 132.5	— 87.5	c	sl. sol.
P <sub>2</sub> H <sub>4</sub>	1. 1.01	< — 10	57.5 (735 mm.)	c	v. sl. sol.
PI <sub>3</sub>		61		r	hydr.
P <sub>2</sub> I <sub>4</sub>		110		r	hydr.
PH <sub>4</sub> I			s. 61.8 (708)	c	sol.
P <sub>2</sub> S <sub>3</sub>		290	490	gy-y	d.
P <sub>2</sub> S <sub>5</sub>	2.03	276	514	gy-y	d.
P <sub>4</sub> S <sub>3</sub>	2.03	172.5	407.5	y	not. sol. d. by hot water
PSBr <sub>3</sub>	2.85	38.0			hydr.
<i>Platinum</i>					
Pt	21.45	1770	4407	sil-gy	not sol.
PtO		555		v-bk	v. sl. sol.
PtO <sub>2</sub>		430		bk	v. sl. sol.
Pt(OH) <sub>2</sub>		d.		bk	v. sl. sol.
PtBr <sub>2</sub>		d. 300		br	v. sl. sol.
PtBr <sub>4</sub>		d. 180			0.41(20°)
PtCl <sub>2</sub>	5.87	d. 581		gr-gy	v. sl. sol.
PtCl <sub>4</sub> ·8H <sub>2</sub> O	2.43	d.		r	v. sol.

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
H <sub>2</sub> PtCl <sub>6</sub> ·H <sub>2</sub> O	2.43	d.		r-br	sol.
PtI <sub>2</sub>		d. 325		bk	v. sl. sol.
PtI <sub>4</sub>		d. 100		br-bk	sol.
PtP <sub>2</sub> O <sub>7</sub>	4.85	d. > 600		gr-y	v. sl. sol.
PtS	8.90	d.		bk	v. sl. sol.
PtS <sub>2</sub>	5.27	d.		y-br	v. sl. sol.
Pt(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O				y	sol.
<i>Potassium</i>					
K	0.86	63.5	774	sil	giv. KOH + H <sub>2</sub>
K <sub>2</sub> O	2.32			gy	giv. KOH
KO <sub>2</sub>		> 280		y	giv. KOH + H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>
KH	0.80	d.		c	giv. KOH + H <sub>2</sub>
KOH	2.04	360	1327	c	2 aq. 53(22°), 1 aq. 66 (110°)
KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	1.8	292		c	255 g./100 g. H <sub>2</sub> O(20°)
K <sub>2</sub> Al <sub>2</sub> O <sub>4</sub> ·3H <sub>2</sub> O				c	sol.
KSbO <sub>3</sub>				c	sl. sol.
KSbOC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · $\frac{1}{2}$ H <sub>2</sub> O	2.61			c	7.85(25°)
K <sub>3</sub> AsO <sub>4</sub>				c	sol.
KH <sub>2</sub> AsO <sub>4</sub>	2.87	288		c	15.9(6°)
KAsO <sub>2</sub>				c	sol.
KAuCl <sub>4</sub>		357		y	38.2(20°)
K <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·5H <sub>2</sub> O		5 aq. red heat		c	sol. hydr. sl.
KBrO <sub>3</sub>	3.27	d. 370		c	3.1(0°), 11.7(40°)
KBr	2.75	742	1380	c	39.4(20°), 51.2(100°)
K <sub>2</sub> PtBr <sub>6</sub>	4.66	d. > 400			2.0(20°)
K <sub>2</sub> CO <sub>3</sub>	2.29	897		c	2 aq. 53(25°)
KHCO <sub>3</sub>	2.17	d.		c	18.3(0°), 28.1(30°)
KCl	1.99	770	1407	c	22.0(0°), 25.8(25°)
KClO		d.		c	v. sol.
KClO <sub>3</sub>	2.32	368		c	3.2(0°), 9.2(30°)
KClO <sub>4</sub>	2.52	d. 400		c	0.7(0°), 15.8(100°)
K <sub>2</sub> PtCl <sub>6</sub>	3.50	d. 250		y	0.5(0°), 5(100°)
K <sub>2</sub> CrO <sub>4</sub>	2.73	975		y	38.6(20°)
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	2.69	398		r	4.7(0°), 50.5(100°)
K <sub>3</sub> Co(NO <sub>2</sub> ) <sub>6</sub> · $\frac{3}{2}$ H <sub>2</sub> O		d. 200		y	0.09(0°)
KCN	1.52	623		c	v. sol.
KCNO	2.05			c	sol.
KAg(CN) <sub>2</sub>				c	12.5
K <sub>3</sub> Fe(CN) <sub>6</sub>	1.89			r	29.0(15.6°)
K <sub>4</sub> Fe(CN) <sub>6</sub> ·3H <sub>2</sub> O	1.85	3 aq. 70		y	19.7(20°), 39(75°)
KF	2.48	857	1500	c	2 aq. 49(21°)
KBF <sub>4</sub>	2.50	d. 500		c	sol.
3KF·AlF <sub>3</sub>		1035		c	sol.
K <sub>2</sub> SiF <sub>6</sub>	2.66			c	0.12(17.5°), 0.95(100°)
KI	3.12	682	1324	c	59.0(20°)
KI <sub>3</sub>	3.50	45	d. 225	br	sol.
KIO <sub>3</sub>	3.89	560		c	7.5(20°)
KIO <sub>4</sub>	3.62	582		c	0.66(13°)
K <sub>2</sub> MnO <sub>4</sub>		d. 190		d-gr	sol.
KMnO <sub>4</sub>	2.70	d. < 240		pu	7.1(25°), 20(65°)
K <sub>2</sub> MnO <sub>4</sub>		919		c	v. sol.
KNO <sub>2</sub>	1.91	297	d. 350	c	75.8(25°)
KNO <sub>3</sub>	2.11	338	d. 400	c	24.9(20°), 71(100°)
KNH <sub>2</sub>		338		c	hydr.
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	2.13			c	27.4(25°)
K <sub>3</sub> PO <sub>4</sub>		1340		c	sl. sol.
K <sub>2</sub> HPO <sub>4</sub>		d.		c	v. sol.
KH <sub>2</sub> PO <sub>4</sub>	2.34	96	d. > 200	c	25 g./100 g. H <sub>2</sub> O(7°)
K <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	2.33	1090		c	sol.
K <sub>2</sub> HPO <sub>3</sub>		d.		c	v. sol.

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
K <sub>2</sub> SiO <sub>3</sub>		976		c	sol.
K <sub>2</sub> SeO <sub>4</sub>	3.07			c	52.6(18°)
K <sub>2</sub> S	1.80	471		br	sol. hydr.
K <sub>2</sub> S <sub>6</sub>		206		y	v. sol.
K <sub>2</sub> SO <sub>3</sub> ·2H <sub>2</sub> O		d.		c	v. sol.
KHSO <sub>4</sub>	2.35	210		c	v. sol.
K <sub>2</sub> SO <sub>4</sub>	2.66	1074		c	10.75(25°), 19.4(100°)
K <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	2.28	> 300		c	sol.
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>		d. < 100		c	1.6(0°), 5.0(20°)
KCNS	1.89	179		c	v. sol.
K <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·½H <sub>2</sub> O	1.98			c	59(17°)
K <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	3.12	an. 927		c	sol.
KReO <sub>4</sub>	4.89	350		c	1.2(20°)
<i>Praseodymium</i>					
Pr	6.5	921		gy	evol. H <sub>2</sub>
Pr <sub>2</sub> O <sub>3</sub>	6.87			y-gr	sl. sol.
PrCl <sub>3</sub>	4.02	823		gr	51(13°)
Pr <sub>2</sub> S <sub>3</sub>	5.04			br	d.
Pr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	3.72			gr	8 aq. 12.4(18°)
<i>Radium</i>					
Ra	5	960	1140	sil	evol. H <sub>2</sub>
RaBr <sub>2</sub>	5.79	728		y	sol.
RaCl <sub>2</sub>	4.91	1000		c	sol.
<i>Rhenium</i>					
Re		3440		sil	not sol.
Re <sub>2</sub> O <sub>7</sub>	8.2	296	362.4	y	sol.
<i>Rhodium</i>					
Rh	12.5	1955	> 2500	gy-w	not sol.
RhO				gy	v. sl. sol.
Rh <sub>2</sub> O <sub>3</sub>				gy	v. sl. sol.
RhO <sub>2</sub>				br	v. sl. sol.
Rh(OH) <sub>3</sub>		d.		bk	v. sl. sol.
RhCl <sub>3</sub>		d. 475		r	sol. if hydrated
Rh(NO <sub>3</sub> ) <sub>3</sub> ·2H <sub>2</sub> O				r	sol.
Rh <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·12H <sub>2</sub> O				l-y	v. sol.
RhS		d.		bl	v. sl. sol.
<i>Rubidium</i>					
Rb	1.53	39.0	679	sil	giv. RbOH + H <sub>2</sub>
Rb <sub>2</sub> O	3.72	d. 400		c	giv. RbOH
Rb <sub>2</sub> O <sub>2</sub>	3.65	600		y	giv. RbOH + H <sub>2</sub> O <sub>2</sub>
RbO <sub>2</sub>	3.05	280		y	giv. RbOH + H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>
RbOH	3.20	300		c	36.4(30°)
RbBr	3.35	677	1352	c	51.2(16°)
Rb <sub>2</sub> CO <sub>3</sub>		837		c	v. sol.
RbCl	2.76	717	1381	c	47.7(20°)
RbF		833	1410	c	sol.
RbI	3.55	638	1300	c	60(17°)
RbNO <sub>3</sub>	3.11	305		c	34.8(20°)
Rb <sub>2</sub> S	2.91			c	v. sol.
Rb <sub>2</sub> SO <sub>4</sub>	3.61	1060		c	32.5(20°)
<i>Ruthenium</i>					
Ru	12.2	2450	> 2700	gy	not. sol.
Ru <sub>2</sub> O <sub>3</sub>				bl-bk	v. sl. sol.
RuO <sub>2</sub>	7.2			v	v. sl.
RuO <sub>4</sub>	5.77	25.5	100.8 183 mm.	y	sl. sol.
Ru(OH) <sub>3</sub>				bk	v. sl. sol.
RuCl <sub>3</sub>				br	sol.
RuS <sub>2</sub>				bk	v. sl. sol.
RuSi	5.4			w	v. sl. sol.



FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
<i>Scandium</i>					
Sc	2.5	1200	2400	sil	evol. H <sub>2</sub>
Sc <sub>2</sub> O <sub>3</sub>	3.86			c	v. sl. sol.
ScCl <sub>3</sub>		939		c	v. sol.
Sc(NO <sub>3</sub> ) <sub>3</sub>		150		c	sol.
Sc <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2.58			c	5 aq. 28.5(25°)
<i>Selenium</i>					
Se	4.5-4.8	217	680	gy	not sol.
H <sub>2</sub> SeO <sub>3</sub>	3.00	d.		c	62.5(20°)
H <sub>2</sub> SeO <sub>4</sub>	2.95	58		c	v. sol.
SeO <sub>2</sub>	3.95	340	s. 317	c	giv. H <sub>2</sub> SeO <sub>3</sub>
<i>Silicon</i>					
Si	2.4	1427	2287	gy	not sol.
H <sub>2</sub> SiO <sub>3</sub>	2.2			c	sl. sol.
H <sub>4</sub> SiO <sub>4</sub>	1.57			c	sl. sol.
SiO <sub>2</sub> , quartz	2.65	cristobalite 1700		c	v. sl. sol.
SiO <sub>2</sub> , glass	2.20		2230	c	v. sl. sol.
SiBr <sub>4</sub>	2.81	5	153	c	hydr.
SiC	3.17	> 2700	s. 2210 diss.		v. sl. sol.
SiCl <sub>4</sub>	1.148	- 67.6	57	c	hydr.
SiF <sub>4</sub>		- 77	- 94.8		hydr.
SiH <sub>4</sub>	1.068	- 185	- 112	c	sl. sol.
Si <sub>2</sub> H <sub>6</sub>	1.069	- 132.5	- 14.3	c	sl. sol.
Si <sub>3</sub> H <sub>8</sub>	1.0725	- 117	53	c	sl. sol.
Si <sub>4</sub> H <sub>10</sub>	1.079	- 93.5	100	c	sl. sol.
SiI <sub>4</sub>		120.5	290	c	hydr.
<i>Silver</i>					
Ag	10.5	961	2212	sil	not sol.
Ag <sub>2</sub> O	7.14	d. 300		br	0.00215(20°)
Ag <sub>2</sub> O <sub>2</sub>	7.44	d. > 100		bk	v. sl. sol.
AgC <sub>3</sub> H <sub>3</sub> O <sub>2</sub>	3.26	d.		gr	1.021(20°), 2.52(80°)
Ag <sub>2</sub> AsO <sub>3</sub>		d. 150		y	0.00115(20°)
Ag <sub>3</sub> AsO <sub>4</sub>	6.66			d-r	0.00085(20°)
AgBr	6.47	430		l-y	8.4 × 10 <sup>-6</sup>
AgBrO <sub>3</sub>	5.21	d.		c	0.159(20°)
Ag <sub>2</sub> CO <sub>3</sub>	6.08	d. 218		c	0.002
AgClO <sub>3</sub>	4.43	230	d. 270	c	sol.
AgClO <sub>4</sub>	2.81	d. 486		c	84(25°)
AgCl	5.56	455	1564	c	0.00015(20°)
Ag <sub>2</sub> CrO <sub>4</sub>				d-r	0.0025(18°)
Ag <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>		d.		r	0.0083(15°)
AgCN	3.95	350		c	0.00002(25°)
AgCNO	4.00	d.		c	0.003(18°)
Ag <sub>3</sub> Fe(CN) <sub>6</sub>				or	0.00007(20°)
Ag <sub>4</sub> Fe(CN) <sub>6</sub> ·H <sub>2</sub> O				y	v. sl. sol.
AgNO <sub>2</sub>	4.45	d. 140		c	0.4(25°)
AgF	5.85	435		y	4 aq. 57.5(15°)
AgI	5.67	557	1506	y	2.5 × 10 <sup>-7</sup> (25°)
AgIO <sub>3</sub>	5.52	> 200		c	0.0038(18°)
AgN <sub>3</sub>		exp. 251.5		bk	v. sl. sol.
AgNO <sub>3</sub>	4.35	209	d. 444	c	68.3(20°)
Ag <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	5.03	ex. 140		c	0.004(25°)
AgMnO <sub>4</sub>		d.		bl-bk	1.5(25°)
Ag <sub>2</sub> P <sub>3</sub>	4.63	d.		gy	v. sl. sol.
AgPO <sub>3</sub>	6.37	482			v. sl. sol.
Ag <sub>3</sub> PO <sub>4</sub>	6.37	849		l-y	0.0006(25°)
Ag <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	5.31	585		c	v. sl. sol.
Ag <sub>2</sub> S	7.32	842		bk	v. sl. sol.
Ag <sub>2</sub> SO <sub>3</sub>		d. 100		c	sl. sol.
Ag <sub>2</sub> SO <sub>4</sub>	5.45	657		c	0.8(25°)

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
AgCNS				c	0.00002(25°)
<i>Sodium</i>					
Na	0.97	97.5	892	sil	giv. NaOH & H <sub>2</sub>
Na <sub>2</sub> O	2.27			gy	giv. NaOH
Na <sub>2</sub> O <sub>2</sub>		d. 30		y-w	giv. NaOH & HO <sub>2</sub> <sup>-</sup>
NaOH	2.13	322	1378	c	1 aq. 51.7(25°)
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	1.53	324		c	46 g./100 g. H <sub>2</sub> O(20°)
NaAlO <sub>2</sub>		1650		c	sol.
NaSb(OH) <sub>3</sub>				c	0.03(12°)
Na <sub>3</sub> AsO <sub>4</sub> ·12H <sub>2</sub> O	1.76	86.3		c	10.4(17°)
Na <sub>2</sub> HAsO <sub>4</sub> ·12H <sub>2</sub> O	1.72	28		c	27(21°)
Na <sub>2</sub> HAsO <sub>3</sub>	1.87			c	v. sol.
NaBO <sub>2</sub>		966	> 1400	c	sol.
Na <sub>2</sub> BO <sub>7</sub> ·10H <sub>2</sub> O	1.73	75	d. 200	c	1.6(10°) 5 aq. 34(100°)
NaBr	3.20	747	1390	c	2 aq. 47.5(20°)
NaBrO <sub>3</sub>	3.34	381		c	27.7(20°)
Na <sub>2</sub> CO <sub>3</sub>	2.53	854		c	
Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O	1.55			c	31(100°)
Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O	1.46			c	23.0(25°)
NaHCO <sub>3</sub>	2.20			c	8.8(20°)
NaClO <sub>3</sub>	2.49	255		c	50(20°)
NaClO <sub>4</sub>		482		c	sol.
NaCl	2.16	800	1465	c	26.4(20°), 28.2(100°)
NaClO·2.5H <sub>2</sub> O		57.5		c	v. sol.
Na <sub>2</sub> PtCl <sub>4</sub> ·4H <sub>2</sub> O		d. 100		r	sol.
Na <sub>2</sub> PtCl <sub>6</sub> ·6H <sub>2</sub> O	2.50			r	sol.
Na <sub>2</sub> CrO <sub>4</sub> ·10H <sub>2</sub> O	1.48			y	33.4(10°)
Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	2.52	320		r	64.3(20°)
NaCN		562	1496	c	v. sol.
NaCu(CN) <sub>2</sub>	1.01	d. 100		c	sol.
Na <sub>3</sub> Fe(CN) <sub>6</sub> ·H <sub>2</sub> O				r	sol.
Na <sub>4</sub> Fe(CN) <sub>6</sub> ·10H <sub>2</sub> O	1.46			y	20.07(25°)
Na <sub>2</sub> Fe(CN) <sub>5</sub> NO					
·2H <sub>2</sub> O	1.72			r	v. sol.
Na <sub>2</sub> CbO <sub>3</sub>	4.19			l-y	sol.
NaF	2.79	992	1700	c	4.3(18°)
3NaF·AlF <sub>3</sub>	2.90	1000		c	sol.
Na <sub>2</sub> SiF <sub>6</sub>	2.68			c	0.65(17.5°), 2.4(100°)
NaCHFO <sub>2</sub>	1.92	253		c	46.9(21°)
NaH	0.92			c	giv. NaOH + H <sub>2</sub>
NaI	3.67	662	1300	c	2 aq. 64.8(25°)
NaIO <sub>3</sub>	4.27	d.		c	2.4(0°), 25.3(100°)
Na <sub>2</sub> MnO <sub>4</sub> ·10H <sub>2</sub> O		d.		gr	v. sol.
Na <sub>2</sub> MoO <sub>4</sub>		687		c	2 aq. 39.4(20°)
NaNH <sub>2</sub>		210		c	hydr.
NaNO <sub>2</sub>	2.17	271	d. 320	c	44.9(15°)
NaNO <sub>3</sub>	2.57	310		c	46.8(20°)
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>				c	3.1(15°), 4.3(50°)
NaH <sub>2</sub> PO <sub>2</sub> ·H <sub>2</sub> O				c	sol.
Na <sub>2</sub> HPO <sub>3</sub> ·5H <sub>2</sub> O				c	sol.
NaPO <sub>3</sub>	2.48	988		c	sl. sol.
NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	2.07	d. 190		c	2 aq. 48(25°)
Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	1.52	34.6		c	11(25°)
Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	1.62	an. 1340		c	v. sol.
Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> ·10H <sub>2</sub> O	1.82	an. 970		c	3.1(0°), 23.1(80°)
NaKCO <sub>3</sub> ·6H <sub>2</sub> O	1.63	6 aq. 100		c	v. sol.
Na <sub>2</sub> SeO <sub>4</sub>	3.10			c	10 aq. 30.3(20°)
Na <sub>2</sub> SiO <sub>3</sub>		1088		c	v. sol.
Na <sub>2</sub> Si <sub>4</sub> O <sub>9</sub>				c	v. sol.
Na <sub>2</sub> Sn(OH) <sub>6</sub>				c	37(20°)
Na <sub>2</sub> S	1.85	920		y	9 aq. 16.2(22°)

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
Na <sub>2</sub> S <sub>8</sub>		251.8		y	v. sol.
Na <sub>2</sub> SO <sub>3</sub>	2.63			c	7 aq. 20.1(18°)
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	1.68	d. 48.0		c	41.2(20°), 2 aq. 73(100°)
NaHSO <sub>4</sub>	2.74	> 315		c	v. sol.
Na <sub>2</sub> SO <sub>4</sub>	2.69	884		c	29.9(100°)
Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	1.46	d. 32.4		c	16.1(20°)
NaCNS		323		c	v. sol.
Na <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·2H <sub>2</sub> O	1.82			c	v. sol.
Na <sub>3</sub> VO <sub>4</sub>		ca. 866		c	sol.
Na <sub>2</sub> WO <sub>4</sub>	4.18	702		c	2 aq. 42.2(20°)
NaMnO <sub>4</sub> ·3H <sub>2</sub> O	2.46	d. 170		pu	v. sol.
NaReO <sub>4</sub>		300		c	20(20°)
<i>Strontium</i>					
Sr	2.6	757	1384	sil	giv. Sr(OH) <sub>2</sub> + H <sub>2</sub>
SrO	4.7			gy-w	giv. Sr(OH) <sub>2</sub>
Sr(OH) <sub>2</sub>	3.62			c	8 aq. 0.4(0°), 21.8(100°)
SrBr <sub>2</sub>	4.22	643		c	
SrBr <sub>2</sub> ·6H <sub>2</sub> O	2.36	d. 20		c	50.0(20°)
SrCO <sub>3</sub>	3.70	1497 (60 atm.)		c	0.001(18°)
SrCl <sub>2</sub>	3.05	872		c	
SrCl <sub>2</sub> ·6H <sub>2</sub> O	1.93	d. 61		c	35.0(20°), 45.4(60°)
Sr(ClO <sub>3</sub> ) <sub>2</sub>	3.15	d. 120		c	63.6(18°)
SrCrO <sub>4</sub>	3.89			y	0.11(15°)
SrF <sub>2</sub>	2.44	1400		c	0.0017(18°)
SrI <sub>2</sub>	4.54	402		c	
SrI <sub>2</sub> ·6H <sub>2</sub> O	4.41			c	64.2(20°)
Sr(NO <sub>3</sub> ) <sub>2</sub>	2.99	570		c	
Sr(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	2.2			c	41.5(20°)
SrC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O		d.		c	0.006(20°)
SrHPO <sub>4</sub>	3.54			c	v. sl. sol.
SrS	3.70			c	sol. hydr.
SrSO <sub>3</sub>		d.		c	0.003(17°)
SrSO <sub>4</sub>	3.96	d. 1580		c	0.01(20°)
SrSiO <sub>3</sub>	3.65	1580		c	v. sl. sol.
<i>Sulfur</i>					
S(M)	1.96	119.0	444.6	y	not sol.
S(R)	2.07	112.8	444.6	y	not sol.
SO <sub>2</sub>	1.143	- 72.7	- 10	c	10.0(20°), 4.5(50°)
SO <sub>3</sub> , α	1.192	16.83	44.8	c	g. H <sub>2</sub> SO <sub>4</sub>
H <sub>2</sub> SO <sub>4</sub>	1.183	10.49		c	v. sol.
H <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	1.184	8.62	290	c	v. sol.
H <sub>2</sub> SO <sub>4</sub> ·2H <sub>2</sub> O	1.165	- 38.9	167	c	v. sol.
H <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	1.19	35.0	d.	c	g. H <sub>2</sub> SO <sub>4</sub>
SOBr <sub>2</sub>	1.268	- 50	139.5	or-r	giv. SO <sub>2</sub> + HBr
SOClBr	1.231		115 d.	y	d.
SCl <sub>4</sub>		- 30		y-br	d.
S <sub>2</sub> Cl <sub>2</sub>	1.167	- 80	138	y-r	giv. HCl + S + H <sub>2</sub> S <sub>2</sub> O <sub>4</sub> slowly
SOCl <sub>2</sub>	1.163	- 104	75.4	c	giv. SO <sub>2</sub> + HCl
SO <sub>2</sub> Cl <sub>2</sub>	1.166	- 54.1	69.1	c	sl. sol. 0°, d. by hot H <sub>2</sub> O
SO <sub>3</sub> SO <sub>2</sub> Cl <sub>2</sub>	1.184	- 37.5	153	c	giv. H <sub>2</sub> SO <sub>4</sub> + HCl slowly
S <sub>2</sub> O <sub>3</sub> Cl <sub>4</sub>		d. 57		w	d.
SF <sub>6</sub>	1.191	- 55(P)	- 63.5	c	sl. sol. hot d.
SOF <sub>2</sub>	1.293	- 110	- 30	c	giv. SO <sub>2</sub> + HF
SO <sub>2</sub> F <sub>2</sub>		- 120(65 mm.)	- 52	c	10 vol./100 vol. H <sub>2</sub> O(9°)
<i>Tantalum</i>					
Ta	16.6	2850	> 4100	gy	not sol.
Ta <sub>2</sub> O <sub>5</sub>	8.73			c	v. sl. sol.
TaBr <sub>5</sub>	4.67	240	320	y	sol. hydr.
TaCl <sub>5</sub>	3.68	221	242	y	sol. hydr.
TaF <sub>5</sub>	4.74	96.8		c	sol. hydr.

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
<i>Tellurium</i>					
Te, $\alpha$	6.24	453	1087	gy	not sol.
H <sub>2</sub> TeO <sub>3</sub>	3.05	d. 40		c	sl. sol.
H <sub>6</sub> TeO <sub>8</sub>	3.05			c	30(18°)
TeO <sub>2</sub>	5.89		s. 450	y	giv. H <sub>2</sub> TeO <sub>3</sub>
TeO <sub>3</sub>	5.08	d.		c	giv. H <sub>6</sub> TeO <sub>8</sub>
TeBr <sub>2</sub>		ca. 280	339	gy	hydr.
TeCl <sub>2</sub>	7.05	175	324	bk	hydr. to TeO
TeCl <sub>4</sub>		214	392	w	hydr.
TeF <sub>6</sub>			- 38.6	c	hydr.
TeI <sub>2</sub>				bk	hydr. to TeO
TeI <sub>4</sub>	8.40	259		d-br	hydr. slowly
<i>Thallium</i>					
Tl	11.85	302.5	1457	bl-w	not sol.
Tl <sub>2</sub> O		300	d. 1855	y	giv. TlOH
Tl <sub>2</sub> O <sub>3</sub>	br. 9.65 bk. 10.19	759		br bk	v. sl. sol.
TlOH			139 diss.	y	343 g./liter (18.5°)
Tl(OH) <sub>3</sub>		> 340		br	v. sl. sol.
TlBr	7.56	460	815	l-y	0.05(20°)
TlBrO <sub>3</sub>				c	0.35(20°)
Tl <sub>2</sub> CO <sub>3</sub>	7.11	273		c	3.8(15°), 20(100°)
TlCl	7.00	427	807	c	0.34(20°), 1.9(90°)
TlClO <sub>4</sub>	4.89	501		c	17(30°)
TlF			300	c	44(15°)
TlI	7.09	440	824	y	0.0064(20°), 0.1(100°)
TlN <sub>3</sub>		334		y	v. sl. sol.
TlNO <sub>3</sub>	5.55	207	430	c	3.8(0°), 23.3(50°)
(NH <sub>4</sub> ) <sub>3</sub> TlCl <sub>6</sub> ·2H <sub>2</sub> O	2.39			c	sol.
Tl <sub>3</sub> PO <sub>4</sub>	6.89			c	0.5(15°)
Tl <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	6.79	> 120		c	sol.
Tl <sub>2</sub> S	8.0	449		bl-bk	0.02(20°)
Tl <sub>2</sub> SO <sub>4</sub>	6.77	632		c	4.64(20°), 15.6(100°)
Tl <sub>2</sub> Se		340		gy	sl. sol.
<i>Thorium</i>					
Th	11.2	1845	> 3000	gy	evol. H <sub>2</sub>
ThO <sub>2</sub>	9.69	> 2800		c	v. sl. sol.
Th(OH) <sub>4</sub>		d.		c	v. sl. sol.
ThBr <sub>4</sub>	5.67		s. 610	c	v. sol.
ThCl <sub>4</sub>	4.59	820		c	v. sol.
Th <sub>3</sub> (PO <sub>3</sub> ) <sub>4</sub>	4.08			c	sl. sol.
ThS <sub>2</sub>	6.8	d.		y	v. sl. sol.
Th(SO <sub>4</sub> ) <sub>2</sub> ·9H <sub>2</sub> O	2.77	d. 406		c	1.36(20°)
ThO <sub>2</sub> ·SiO <sub>2</sub>	5.3			c	v. sl. sol.
K <sub>2</sub> ThF <sub>6</sub> ·H <sub>2</sub> O				c	6 × 10 <sup>-6</sup> (25°)
<i>Tin</i>					
Sn	w. 7.31 g. 5.75	231.8	2270	w	not sol.
H <sub>2</sub> Sn(OH) <sub>6</sub>				c	v. sl. sol.
H <sub>2</sub> SnCl <sub>6</sub> ·6H <sub>2</sub> O	1.93			c	sol.
SnO	6.95			bk-& d-gr	v. sl. sol.
SnO <sub>2</sub>	7.0	1127		gy-w	v. sl. sol.
Sn(OH) <sub>2</sub>		d. 160		w	1.6 × 10 <sup>-4</sup> (25°)
SnBr <sub>2</sub>	5.12	232	620	y	sol.
SnBr <sub>4</sub>	l. 3.34	30.0	202	c	hydr.
SnCl <sub>2</sub>		246.8	623	c	
SnCl <sub>2</sub> ·2H <sub>2</sub> O	2.7	d. 37.7	d.	c	70.1(25°)
SnCl <sub>4</sub>	l. 2.23	- 33.2	113	c	sol. hydr.
SnI <sub>2</sub>	5.21	320	720	r	0.77(20°), 3.9(100°)
SnI <sub>4</sub>	4.46	143.5	340	r-y	hydr.

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
SnS	5.08	880	1230	br	v. sl. sol.
SnS <sub>2</sub>	4.5			y	v. sl. sol.
SnSO <sub>4</sub>		d. 360		c	16(20°)
Sn(SO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O				c	sol. hydr.
<i>Titanium</i>					
Ti	4.5	1800	> 3000	gy	not sol.
TiO				bl-bk	giv. Ti(OH) <sub>2</sub>
Ti <sub>2</sub> O <sub>3</sub>	4.6	2130		vi	v. sl. sol.
TiO <sub>2</sub> (Rutile)	4.26	1825		bl	v. sl. sol.
TiO <sub>2</sub> ·2H <sub>2</sub> O		d.		w	v. sl. sol.
TiBr <sub>4</sub>		38.2	230	y	sol. hydr.
TiCl <sub>2</sub>				bk	sol.
TiCl <sub>3</sub>		d. 440		v	sol.
TiCl <sub>4</sub>	1.7	- 23	136	l-y	sol. hydr.
TiN	5.18	2930		br-r	not sol.
TiS <sub>2</sub>				gr	hydr. slowly
<i>Tungsten</i>					
W	19.3	3387	5927	gy-bk	not sol.
H <sub>2</sub> WO <sub>4</sub>	5.5			y	v. sl. sol.
WO <sub>2</sub>	12.11			br	v. sl. sol.
WO <sub>3</sub>	7.16	> 2130		y	v. sl. sol.
WC	15.7	2777	6000	gy	not sol.
W <sub>2</sub> C	16.06	2877	6000	gr	not sol.
WCl <sub>2</sub>				gy	sol. hydr.
WCl <sub>4</sub>	4.62	d.		gy	sol. hydr. to WO <sub>2</sub>
WCl <sub>5</sub>	3.87	248	275.6	bk	sol.
WCl <sub>6</sub>	3.52	275	346.7	d-bl	hydr. to WO <sub>3</sub>
WBr <sub>5</sub>		276	333	d-br	sol.
WF <sub>6</sub>		- 0.4	17.3	c	hydr.
WI <sub>2</sub>	6.9			br	hydr.
WI <sub>4</sub>	5.2			bk	sol. hydr. to WO <sub>2</sub>
WS <sub>2</sub>	7.5	d. 1250		gy	not sol.
<i>Uranium</i>					
U	18.7	< 1850	3500	w	evol. H <sub>2</sub>
UO <sub>2</sub>	10.9	2176		bk	v. sl. sol.
UO <sub>3</sub>	7.29			y	v. sl. sol.
U <sub>2</sub> O <sub>3</sub>	7.31			gr	v. sl. sol.
UBr <sub>4</sub>	4.84			bk	v. sol.
UC <sub>2</sub>	11.3	2260	4100	gy	giv. UO <sub>2</sub> + hyd-carbn.
UCl <sub>4</sub>	4.72			gr	sol.
UF <sub>6</sub>	4.68	69.2 (2 atm.)	s. 56	y	sol. hydr.
UI <sub>4</sub>	5.6	s. 500		bk	sol.
UO <sub>2</sub> (IO <sub>3</sub> ) <sub>2</sub>	5.2	d. 250		y	0.12(18°)
US <sub>2</sub>		> 1100		gy	v. sl. sol.
U(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O		4 aq., 300		gr	9.8(24°)
UO <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	2.89	d. 275		y	sol.
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	2.74	60	118	y	57(25°)
UO <sub>2</sub> (HPO <sub>4</sub> )·4H <sub>2</sub> O				y	not sol.
UO <sub>2</sub> S		d.		br	sl. sol.
UO <sub>2</sub> SO <sub>4</sub> ·3H <sub>2</sub> O	3.28	d. 100		y	14.8(15.5°)
<i>Vanadium</i>					
V	5.96	1710	3000	l-gy	not sol.
HVO <sub>3</sub>				y	sl. sol.
H <sub>4</sub> V <sub>2</sub> O <sub>7</sub>				br	sl. sol.
VO	5.76			gr	v. sl. sol.
VO <sub>2</sub>	4.40	> 1755		d-gr	v. sl. sol.
V <sub>2</sub> O <sub>3</sub>	4.87	1970		bk	v. sl. sol.
V <sub>2</sub> O <sub>5</sub>	3.56	800		or & y	giv. HVO <sub>3</sub>
VC	5.4	2830	5900	gy	not sol.
VCl <sub>2</sub>	3.23			gr	sol.
VCl <sub>3</sub>	3.00			pk	sol.

FORMULA	DENSITY	MELTING POINT °C.	BOILING POINT °C.	COLOR	SOLUBILITY IN WATER
VCl <sub>4</sub>	1. 1.82	— 109	148.5	r	sol. giv. VOCl <sub>2</sub>
VF <sub>5</sub>	2.18		111.2	y	hydr.
VN	5.63	2050		gr-br	not sol.
V <sub>2</sub> S <sub>3</sub>	4.7			bk	v. sl. sol.
V <sub>2</sub> S <sub>5</sub>	3.000			bk	v. sl. sol.
VOCl <sub>3</sub>	1.82	> 15	127	y	hydr.
V <sub>2</sub> Si	5.48			w	not sol.
<i>Xenon</i>					
Xe	s. 2.7	— 140	— 108	c	21.8 cc./100 cc. H <sub>2</sub> O(0°)
<i>Ytterbium</i>					
Yb					evol. H <sub>2</sub>
Yb <sub>2</sub> O <sub>3</sub>	9.17			c	v. sl. sol.
YbCl <sub>3</sub> ·6H <sub>2</sub> O	2.57			gr	v. sol.
Yb <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	3.79			c	8 aq. 30.7(0°), 4.5(100°)
Yb <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·10H <sub>2</sub> O				c	0.000033(25°)
<i>Yttrium</i>					
Y	5.57	1490	2500	gy-bl	evol. H <sub>2</sub>
Y <sub>2</sub> O <sub>3</sub>	4.84	2410		c	v. sl. sol.
Y(OH) <sub>3</sub>		d.		y	v. sl. sol.
YCl <sub>3</sub> ·H <sub>2</sub> O		160		c	6 aq. 43(25°)
Y(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	2.68			c	57.4(22.5°)
Y <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·8H <sub>2</sub> O	2.56			c	aq. 6.7(25°)
<i>Zinc</i>					
Zn	7.14	419.5	907	gy	not sol.
ZnO	5.47	1965		w	0.0042(18°)
Zn(OH) <sub>2</sub>	3.05	d. 125		c	0.00042
Zn(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	1.73	237		c	23.7(20°)
ZnBr <sub>2</sub>	4.22	394	650	c	82.5(25°)
ZnClO <sub>3</sub>	4.44	d. 300		c	0.001(25°)
ZnCl <sub>2</sub>	2.91	283	732	c	78.6(20°)
ZnCl <sub>2</sub> ·2NH <sub>3</sub>		210.8	d. 271	c	giv. Zn(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup>
Zn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	2.15	60		c	v. sol.
Zn(CN) <sub>2</sub>		d. 800		c	sol.
Zn <sub>2</sub> Fe(CN) <sub>6</sub> ·3H <sub>2</sub> O			d.	c	v. sl. sol.
ZnF <sub>2</sub>	4.84	872		c	1.6(18°)
ZnI <sub>2</sub>	4.66	446	624	c	83.1(22°)
Zn(IO <sub>3</sub> ) <sub>2</sub>	4.98	d.		c	0.87 in "cold" H <sub>2</sub> O
Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	2.06	36.4		c	55.9(25°)
ZnC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O	2.56	d. 100		c	0.0007(25°)
Zn <sub>3</sub> P <sub>2</sub>	4.55	> 420	1100	gy	not sol. giv. PH <sub>3</sub> with H <sup>+</sup>
Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	4.0	900		c	v. sl. sol.
Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub>				c	v. sl. sol.
ZnS	4.08	1645	s. 1185	c	0.0007(18°)
ZnSO <sub>4</sub>	3.74	d. 740		c	
ZnSO <sub>4</sub> ·7H <sub>2</sub> O	1.97		d. 280	c	36.7(25°)
ZnO·SiO <sub>2</sub>	3.52	1437		c	v. sl. sol.
ZnTe	5.54	1238.5		r	v. sl. sol.
<i>Zirconium</i>					
Zr	6.4	1700	> 2900	gy	not sol.
ZrO <sub>2</sub>	5.49	2715		w	v. sl. sol.
Zr(OH) <sub>4</sub>	3.25	2 aq. 550		w	0.02
ZrCl <sub>4</sub>			331	c	sol. hydr.
ZrF <sub>4</sub>	4.43	sub		c	1.3
Zr(NH <sub>4</sub> ) <sub>3</sub> F <sub>7</sub>				c	sl. sol.
Zr(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O		d. 100		c	sol.
Zr(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O				c	v. sol.
ZrO <sub>2</sub> SiO <sub>2</sub>	4.5	2500		c	v. sl. sol.



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## PERIODIC TABLE

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# INTERNATIONAL ATOMIC WEIGHTS

1939

	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT		SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	163.5	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0081	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.84	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	175.0	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22



